NMR STUDIES OF THE EXCHANGE REACTIONS OF CH_3CNBX_3 WITH EXCESS CH_3CN

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TO MY PARENTS

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NMR Studies of the Exchange Reactions of $CH_3CN.BX_3$ with excess CH_3CN

Proton NMR studies reveal that the rate of exchange of the $CH_3CN.BBr_3$ and $CH_3CN.BCl_3$ adducts and possibly the $CH_3CN.BF_3$ adduct as well with excess base is governed by a first order rate of dissociation of the adducts.

Under similar solvent conditions at a given temperature, we have determined that the relative rates of dissociation vary as

$$CH_3CN.BF_3 > CH_3CN.BCl_3 > CH_3CN.BBr_3$$

and this agrees with previous experimental evidence that the strength of the donor-acceptor bond varies as

$$CH_3CN.BBr_3 > CH_3CN.BCl_3 > CH_3CN.BF_3$$

We also found that our particular coordinating solvent systems influenced the rate of dissociation of the adducts as well as the activation energy for exchange. This has been attributed to the formation of a solvent cage intermediate.

By varying the coordinating solvent concentration of the media and graphically extrapolating for the inert solvent condition, we have obtained activation energies for exchange which correspond quite well with the dissociation energies of the adducts as calculated by previous workers.

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Introduction

Exchange reactions between molecular complexes and excess acid or base are well known and have been extensively surveyed in the literature(1). Since the exchange mechanism will, in some way involve the breaking of the labile donor-acceptor bond, it follows that a discussion of the factors relating to bonding in molecular complexes will be relevant.

In general, a strong Lewis base and a strong Lewis acid form a stable adduct provided that certain stereochemical requirements are met.

A strong Lewis base has the following characteristics (1),(2)

(i) high electron density at the donor site.
(ii) a non-bonded electron pair which has a low ionization potential
(iii) electron donating substituents at the donor atom site.
(iv) facile approach of the site of the Lewis base to the acceptor site as dictated by the steric hindrance of the substituents.

Examples of typical Lewis bases are ethers, nitriles, ketones, alcohols, amines and phosphines.

For a strong Lewis acid, the following properties are important:-

(i) low electron density at the acceptor site.
(ii) electron withdrawing substituents.

(iii) substituents which do not interfere with the close approach of the Lewis base.

(iv) availability of a vacant orbital capable of accepting the lone electron pair of the donor atom.

Examples of Lewis acids are the group III and IV halides such as MX_3 (M=B, Al, Ga, In) and MX_4 (M=Si, Ge, Sn, Pb).

The relative bond strengths of molecular complexes have been investigated by:-

(i) dipole moment measurements (3).

(ii) shifts of the carbonyl peaks in the I.R. (4),(5),(6).

(iii) NMR chemical shift data (4),(7),(8),(9).

(iv) U.V. and visible spectrophotometric shifts (10),(11).

(v) equilibrium constant data (12), (13).

(vi) heats of dissociation and heats of reactions (14), (16), (17), (18), (19).

Many experiments have been carried out on boron trihalides in order to determine their relative acid strengths. Using pyridine, nitrobenzene, acetonitrile and trimethylamine as reference Lewis bases, it was found that the acid strength varied in order: $BBr_3 > BCl_3 > BF_3$. For the acetonitrile-boron trihalide and trimethylamine boron trihalide complexes in nitrobenzene, an NMR study (7) showed that the shift to lower field was greatest for the BBr_3 adduct and smallest for the BF_3 which is in agreement with the acid strengths.

If electronegativities of the substituents were the only important effect, and since $\chi_F > \chi_{Cl} > \chi_{Br}$, one would expect the electron density at the boron nucleus to vary as $BF_3 < BCl_3 <$ BBr_3 and therefore, the acid strength would vary as $BF_3 > BCl_3 > BBr_3$: However, for the boron trihalides, the trend is in the opposite direction as determined experimentally. Considerable back-bonding (20), (21) between the halogen and the boron atoms has been proposed as the predominating factor, i.e. $p\pi - p\pi$ back-bond between a lone electron pair on the halogen and the vacant orbital on the boron site.

The degree of back-bonding varies inversely as the boron halogen distance and one would therefore expect the B-F bond to exhibit greater back-bonding character than the B-Cl or B-Br bonds. Since back-bonding transfers electron density from substituent to the boron atom site, this process would be expected to weaken the Lewis acid strength. This explains the Lewis acid strength increasing in the order $BF_3 < BCl_3 < BBr_3$.

When the acetonitrile boron trihalide complex is formed, the boron atom undergoes a change of hybridization from sp^2 to sp^3. From a linear relationship between the heat of formation of ethyl acetate adducts and the shift in the carbonyl I.R. stretch, Drago (22) et al have proposed that the angular distortion of the X-B-X bonds from sp^2 (120°) to sp^3 (109°) hybridization is proportional to the amount of charge transferred, i.e. to the nature of the base, and they have rejected the earlier concept of reorganization energy in explaining the formation of the adduct bond (19).

Therefore in the complex, residual backbonding still exists in the same relative proportions as for the free Lewis acid since the amount of π backbonding which is lost on complex formation is only dependent on the particular Lewis base.

These bonding effects will influence the relative rates of exchange of the BX_3 adducts. A priori, one would expect the adduct which is most weakly bonded to exchange at the fastest rate.

The donor acceptor bond strengths of many stable molecular complexes have been measured and vary from 15 to 40 Kcal mole^{-1}. Due to solvation effects, the energy required for dissociation in solution is considerably reduced. For example, for the gas phase dissociation of solid CH_3CNBX_3 adducts, the heats of dissociation as calculated by Laubengayer et al (14) and by Miller and Onyszchuk are (15) 39.4 Kcal for the BBr_3 adduct, 33.8 for the BCl_3 and 26.5 for the BF_3. In solution however, Lockhart and Blackborow have calculated dissociation energies of 19.6 Kcal for the BBr_3 adducts, 18.1 for the BCl_3 and using similar methods an approximate value of 11 Kcal for the BF_3 adducts was calculated as part of this work. (23)

NMR and Exchange Reactions (24)

Nuclei which have non-zero nuclear spins (i.e., all except those with even numbers of both protons and neutrons) will give rise to NMR signals. The strength of the NMR signal is a function of the relative abundance of the isotope of a given element as well as its relative sensitivity to resonance. Fortunately many nuclei which are naturally abundant also are NMR active - H^1 (99.98%), F^{19} (100%), B^{11} (81.2%), N^{14} (99.6%), P^{31} (100%). Adducts containing these nuclei can be investigated using NMR techniques. Most of the NMR work has been done on H^1 resonance, while F^{19} ranks next in importance. The ^{11}B NMR of some adducts containing boron have been studied by Muetterties et al (24), (25) and by Hamilton, Hartman and Miller (26) and Mooney (27).

In proton NMR, the chemical shift of adducts is mainly a function of the diamagnetic term. The chemical shift of a proton is related to the electron density around it and is given by the relationship

$$\delta = \frac{H - H_{st}}{H_o}$$

where δ = chemical shift of proton
H = effective magnetic field which the proton experiences due to electron shielding
H_{st} = magnetic field strength of internal or external standard
H_o = applied magnetic field

The greater the electron density, the greater the shielding of the nucleus from the applied magnetic field, hence the greater the field required to observe resonance.

If B is a Lewis base containing one type of magnetically equivalent protons, then neglecting heteronuclear coupling, only one peak will be observed in the NMR. But if B is a constituent of a 1:1 molecular complex A←B, then on the formation of the donor acceptor bond, a certain amount of electronic charge must also be removed from the protonic environment by an inductive effect. Thus, the molecular complex A←B will be expected to exhibit a peak downfield with respect to B.

In nitrobenzene, CH_3CN has a signal at 123 cps while for the $CH_3CN.BBr_3$ adduct it is 187 cps (7) downfield from the TMS reference.

If AB and B are together in the same sample tube at room temperature, then there are two possibilities. The sample may give two distinct peaks which may or may not vary significantly with temperature, depending on the value of the equilibrium constant and its temperature dependence. Alternatively, a rapid exchange process may occur and only one peak is observed, in a position between non-exchanging AB and B. That is, the chemical environments of the protons in AB and B are being averaged out by some form of exchange mechanism. This has been attributed to the fast rate of rupture of the AB bond and the subsequent formation of adduct species with the free base.

i.e., stoichiometrically as

$$AB + B^* = AB^* + B.$$

but both first and second order mechanisms will lead to the same collapsed peak system.

At any instant, this exchange process between B and AB may be occurring so rapidly, that, on the NMR time scale, it is impossible to distinguish between the separated AB and B resources and only one average signal is observed.

The position of this averaged peak ν , is a function of the mole fractions of B and AB as given by the relationships

$$\nu = x_{AB} \nu_{AB} + x_B \nu_B$$

where x_{AB} = mole fraction of AB
ν_{AB} = peak position of AB, no exchange
x_B = mole fraction of free base B
ν_B = peak position of B, no exchange

If by some means, the rate of exchange can be progressively slowed down, it becomes possible to resolve the separate resonances. This can be achieved by lowering the temperature of the sample. If exchange is not observed at room temperature, it may be possible to induce exchange by heating the sample.

As the temperature of the sample is lowered, the common peak broadens out and eventually produces two partially collapsed peaks. Upon further cooling, the two peaks may be completely resolved, appearing at the positions expected for the pure compounds. This forms the basis of the NMR method for studying exchange rates at equilibrium. The line widths of the NMR spectra can be related to the mean lifetimes of the adduct and free base.

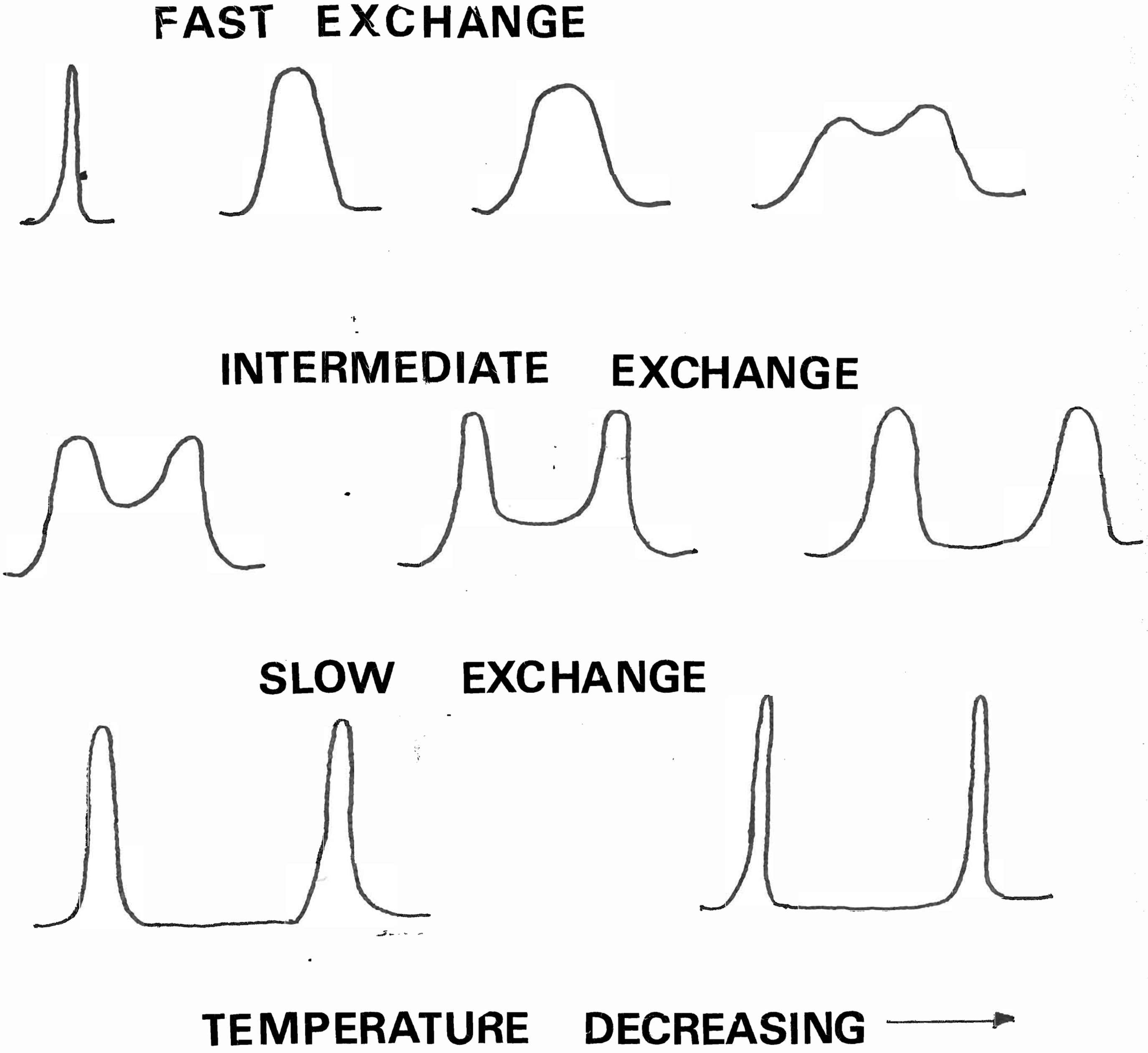
The following diagram (Fig. 1) will illustrate the change of peak shape with temperature and the mathematical equations which apply.

FIGURE (1)

TEMPERATURE DEPENDANCE OF NMR LINE SHAPE

FOR

1:1 SOLUTION OF AB AND B


FAST EXCHANGE
INTERMEDIATE EXCHANGE
SLOW EXCHANGE
TEMPERATURE DECREASING →

Three different exchange conditions are present. For fast exchange above coalescence the following equation applies (28) :

$$\frac{1}{T} = \frac{4(P_{AB})(P_B)(\delta\nu)^2}{(W^* - W'')}$$

where: $\frac{1}{T} \gg 2\pi(\delta\nu)$

T = mean lifetime of B and AB as given by $T = \frac{T_{AB}\ T_B}{T_{AB} + T_B}$

P_{AB}, P_B are the mole fractions of AB and B respectively

$(\delta\nu)$ = separation of signals in absence of exchange

W^* = width at half height of common peak

W'' = natural linewidth of common peak due to effects other than chemical exchange.

For intermediate exchange (28) i.e. at coalescence , , the following equations apply:

$$1 \quad \frac{1}{2T} = \left(\frac{\pi}{2}\right) \left((\delta\nu)^2 - (\delta\nu_e)^2\right)^{\frac{1}{2}}$$

Where $\delta\nu$ = separation of signals in absence of exchange.

$\delta\nu_e$ = separation of signals when partially collapsed

and

$$\frac{1}{2T} = \left(\frac{\pi\delta\nu}{2}\right)) \left(r + (r^2 - r)^{\frac{1}{2}}\right)^{-\frac{1}{2}}$$

where r = ratio of the maximum to the central minimum

These equations apply only for $P_{AB} = P_B$.

Applying these equations by substitution of one set of parameters can lead to large errors. When dealing with exchange rates in this range, a computer simulated full line shape analysis yields far more meaningful results.

When the two peaks are completely (29) separated, slow exchange conditions are met.

$$\frac{1}{T_{AB}} = \pi(\Delta AB - \Delta o)$$

where T_{AB} = mean lifetime of AB before undergoing exchange

ΔAB = width at half height of AB peak

Δo = residual width due to effects other than exchange and is taken as the TMS width at half height for the particular temperature where it is impossible to determine unambiguously from the AB line width.

Similarily

$$\frac{1}{T_B} = \pi(\Delta B - \Delta o)$$

T_B = lifetime of B before exchange.

It is necessary that

$$\frac{1}{T_{AB}}, \frac{1}{T_B} \ll (\delta\nu)$$

for these equations to be used.

Two types of mechanisms can be considered for exchange of adducts with excess base or excess acid - one in which the rate determining step is governed by dissociation of the adduct and the other involving the collision of the adduct with excess base.

It is possible to distinguish between the two molecular mechanisms as follows:-

I Dissociation:

$$AB \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A + B \qquad \text{slow} \quad (1)$$

$$A + B^* \longrightarrow AB^* \qquad \text{fast} \ (2)$$

In this case where slow exchange conditions are met $\frac{1}{T_{AB}}$ and $\frac{1}{T_B}$ can be independently evaluated.

Since T_{AB} is the lifetime of the adduct molecule before exchange $\left(\frac{1}{T_{AB}}\right)$ is the number of exchanges per second and $\left(\frac{AB}{T_{AB}}\right)$ is the rate of exchange in units of moles litre $^{-1}$ sec. $^{-1}$.

From equation (1)

$$\text{Rate of Exchange of AB} = -\frac{d\,(AB)}{dt} = k_1\,(AB)$$

$$\text{Therefore} \qquad \frac{(AB)}{T_{AB}} = k_1\,(AB)$$

$$\frac{1}{T_{AB}} = k_1$$

Similarly from the free base peak width $\frac{(dB)}{dt} = - \frac{d\ (AB)}{dt} = k_1 (AB)$

since the system is at thermal equilibrium

$$\frac{(B)}{T_B} = k_1\ (AB)$$

$$\frac{1}{T_B} = k_1\ \frac{(AB)}{(B)}$$

The theory thus predicts that when the concentration of adduct to free acid or base are varied, $\frac{1}{T_{AB}}$ should be a constant independent of concentration terms while $\frac{1}{T_A}$ or $\frac{1}{T_B}$ divided by the concentration ratios of AB to B or A should be equal to $\frac{1}{T_{AB}}$ (30) (31)

De Roos et al investigated the exchange of $(CH_3)_3$ Ga in Freon II solvent as well as $(CH_3)_3$ In system. (30)
Table I is an extract of their data.

TABLE I

Concentration Dependence for the lifetime of $(CH_3)_3\,Ga.N(CH_3)_2H$ (T_{AB}) and $(CH_3)_3.Ga$ (T_A)

AT 11^o

(AB) M	(A) M	$\frac{1}{T_{AB}}$ sec^{-1}	$\frac{1}{T_A}$ sec^{-1}	$\frac{(AB)}{(A)}$	$\frac{1}{T_A} \Big/ \frac{(AB)}{(A)}$ sec^{-1}
0.258	0.384	9.3	7.85	0.672	11.67
0.407	0.099	8.8	-	4.10	- -
0.361	0.099	9.4	37.7	3.63	10.4
0.302	0.146	9.1	19.2	2.08	8.2
0.241	0.225	9.4	9.6	1.07	9.0
0.099	0.245	10.7	4.08	0.406	10.1
0.227	0.168	10.7	16.3	1.38	11.8
	Av.	9.6			Av. 10.37

Within experimental error $\frac{1}{T_{AB}}$ is independent of concentration and $\frac{1}{T_A} = \frac{1}{T_{AB}} \; {}^{(AB)}\!\big/_{(A)}$. This proves that exchange proceeds by a dissociative mechanism.

The other mechanism postulated for exchange is the collision or second order case.

i.e.- $AB + A^* \underset{}{\overset{k_1}{\rightleftarrows}} A^*B + A$

The equilibrium constant $K_e = 1$

Rate of exchange of AB = $- \frac{d(AB)}{dt} = k_1 (AB)(A)$

$$\frac{(AB)}{T_{AB}} = k_1 (AB)(A)$$

$$\frac{1}{T_{AB}} = k_1 (A)$$

and similarily $\frac{1}{T_A} = k_1 (AB)$

The exchange of $(CH_3)_3Ga.N(CH_3)H_2$ with (30) $(CH_3)_3Ga$ in Freon was shown to proceed via the collision mechanism as seen from the following data, Table 2.

TABLE 2

Determination of Mechanism for $(CH_3)_3$ Ga•N$(CH_3)H_2$ - $(CH_3)_3$ Ga Exchange.

(AB) M	(A) M	$\frac{1}{T_{AB}}$ sec^{-1}	$\frac{1}{T_A}$ sec^{-1}	$\frac{1}{T_{AB}}$ / (A) sec^{-1} M^{-1}	$\frac{1}{T_A}$ / (AB) sec^{-1} M^{-1}
0.364	0.344	25.45	24.19	74.0	66.50
0.436	0.103	7.70	32.25	74.8	74.0
0.0997	0.379	37.00	8.80	97.6	88.3
0.118	0.195	16.93	9.74	86.8	82.5
		Average		78.5	77.8

There is a definite concentration dependence of $\frac{1}{T_{AB}}$ and $\frac{1}{T_A}$ for the second order case.

It is interesting to compare the dimethyl (dissociative) and monomethyl (collision) amines at slow exchange conditions.

The rate constant for dissociation (of the dimethylamine) is much smaller than that for collision (of the monomethylamine). By doing the experiment at different temperature, it is a simple matter to obtain the activation energies of exchange via an Arrhenius plot of lnk versus $\frac{1}{T}$.

Activation Energies for exchange processes can be calculated using the Arrhenius evaluation.

$$k = A \exp \left(- \frac{E_a}{RT} \right)$$

Plots of $\log \frac{1}{T_{AB}}$, $\log \frac{1}{T_B}$ versus $\frac{1}{T}$ will give a straight line with negative slope, the value of the slope equal to $-\left(\frac{E_a}{R}\right)$.

For the dimethylamine system, an activation energy of 19.2 Kcal was obtained which is very close to the adduct dissociation energy of 20 Kcal. For the monomethylamine exchange via the collision mechanism, an activation energy of 10.4 Kcal was obtained although the bond dissociation energy was 20 Kcal as well. The properties described for the dissociation and collision are a basis of distinguishing between these mechanisms. In the overall studies of the ammonia, monomethyl and dimethylamine adducts of trimethylgallium, De Roos et al (30) found that exchange proceeded via dissociation for the dimethylamine while for the monomethylamine and ammonia the collision mechanism was the preferred pathway. They interpreted their findings in terms of the methyl groups causing steric hindrance which essentially prevented the close approach of the gallium atom of the free acid to the nitrogen atom of the adduct for a collision. Therefore, the higher energy dissociative pathway was the preferred mode for exchange. The nitrogen atom of the monomethyl and ammonia adducts was less hindered and hence collision which is a lower energy pathway is favoured. In addition to the activation energy in determining a mechanism for a dissociative pathway, if the transition state is less ordered than the original state, a positive $\Delta S^{\ddagger}$ is expected. The collision mechanism involves a more ordered transition state and a negative $\Delta S^{\ddagger}$ is observed.

Molecular BX_3 Complexes and Exchange Reactions

Blackborow and Lockhart (32) have prepared stable BCl_3 adducts of p-nitroaniline, N-deuterated m-nitroaniline, p-chloroaniline and p-iodoaniline. They showed by proton NMR that in acetonitrile solvent, exchange of the Lewis base proceeds via the weaker borontrichloride complex intermediate. For the reactions of aromatic amines with $CH_3CN.BCl_3$ and $CH_3CN.BBr_3$, in acetonitrile solvent, they found (33) that in the BBr_3 case, the mechanism was dissociation with activation energy of 20± 2 Kcal while for the BCl_3 case, an SN2 mechanism with activation energy 10±2 Kcal (bond dissociation energy 18.1 Kcal) was operative. Rutenberg et al (34), (35), (36) have prepared certain ether BF_3 complexes and studied the BF_3 exchange reactions in mixed ether-BF_3 systems. Two pathways for exchange involving collision mechanisms were observed.

Brownstein (37), (38) et al have investigated the BF_3 adducts of alcohols and ethers and found that exchange processes readily occur in these systems as well. In a recent article, Cowley and Mills (39) looked at a series of boron Lewis acids with nitrogen and phosphorus containing alkyl bases and tabulated results for the exchanging and non-exchanging systems. For the $(CH_3)_3N.B(CH_3)_3$ adduct with excess $B(CH_3)_3$ in CH_2Cl_2, they found that the kinetics proceeded via dissociation of the adduct and their value of 16.9 Kcal for the activation energy was in close agreement with the bond dissociation energy of 17.6 Kcal.

The Roles of the Solvent in Exchange Reactions

In many instances, the solvent merely serves (40) as the reacting media and its suitability is governed by the solubility of the adducts and by its melting point in order that slow exchange conditions be met before the solution freezes out.

Certain solvents, however, which possess weak donor or acceptor properties can be expected to participate to some extent (39). For instance, weakly basic solvents can provide a lower energy pathway for dissociation induced exchange by forming a weak intermediate complex with the Lewis acid of the adduct.

To minimize complications, an inert solvent is usually preferred but in many cases in which solubility of the adduct at low temperature becomes the overriding factor, a weakly coordinating solvent is necessary.

Brown (29) in the study of organolithium exchange processes noted that, in cyclopentane solvent(essentially a non-co-ordinating solvent) the activation energy for dissociation of tetrameric tributyllithium to the dimeric form was 24 Kcal while in ether solvent (which is a weak Lewis base) dissociation of methyllithium tetramer to dimer , the activation energy was only 10 Kcal.

The energy of the metal carbon bond, in both compounds being almost equal in value, Brown attributed this activation energy difference to the complexing properties of the ether.

Normally for a dissociative process, a positive $\Delta S^{\ddagger}$ value is expected. However, Brown observed negative $\Delta S^{\ddagger}$ values and this is rationalized in terms of a solvated complex intermediate.

EXPERIMENTAL

Syntheses of Adducts:

Purification of the CH_3CN and BX_3 and subsequent syntheses of the adducts were performed in a standard glass vacuum system capable of achieving a vacuum of 10^{-3} mm mercury. It was equipped with several U traps for distillation (41) and pressures were measured using a spoon gauge as a null detector.

BCl_3 (7) was purified by trap-to-trap distillation at -78^0 using an acetone-dry ice bath through which the more volatile HCl impurity was pumped off and the BCl_3 retained.

BCl_3 was then distilled off at -60^0 using a chloroform slush bath and collected in a liquid nitrogen cooled trap.

BBr_3 (liquid) was added to a flask containing a few drops of mercury and shaken to remove any Br_2 present. It was further purified by degassing in vacuo and trap-to-trap distillation. BF_3 was purified only by trap to trap distillation. The purity of the Boron trihalides was checked by molecular weight measurements and the I.R. spectra.

Acetonitrile (Baker analysed) was first dried over molecular sieve (4A), then degassed a few times in vacuo.

The adducts were synthesized using similar techniques. A known volume of acetonitrile was first distilled into the reaction vessel cooled by liquid nitrogen followed by the addition of a slight excess of the Lewis acid. The number of moles of Lewis acid was measured using a precalibrated volume at a pressure monitored with the spoon gauge. These mixtures were then allowed to warm up to room temperature to react and form the complex.

Excess acid was then pumped out. Further additions of the acid and base were carried out in the same vessel to nsure a good yield of the product.

The product was then removed into a nitrogen filled dry box (Labconco) with P_2O_5 in small dishes as a drying agent where the contents were transferred to a vacuum sublimation apparatus to further purify the adducts.

In the case of the trifluoride adduct only, it was first necessary to wash the adduct with anhydrous benzene in a Buchner funnel to remove any occluded acetonitrile before sublimation.

The sublimations were carried out using a vacuum sublimation cold finger (14).

The tribromide adduct was sublimed at 150° , the trichloride adduct at 85° and the trifluoride at room temperature.

The purity of the adducts was checked by I.R. and melting points.

Adduct	M.P. found	M.P. Literature	
$CH_3CN.BBr_3$	230	233-235	(41)
$CH_3CN.BCl_3$	194	195-200	(41)
$CH_3CN.BF_3$	128	132-135	(41)

The $CH_3CN.BCl_3$ and $CH_3CN.BBr_3$, were isolated as white opaque granular solids while the $CH_3CN.BF_3$ as colourless transparent crystals.

The adducts were kept in weighing bottles which were stored in small individual dessicators (14) containing P_2O_5 , in the dry box.

Selection of Solvent

Nitrobenzene was a good solvent for all three adducts (7). But since its melting point is 4°C., cooling of the $CH_3CN.BCl_3$-CH_3CN solution resulted in the solution freezing before slow exchange conditions could be obtained. For this system, it was found that a mixed solvent system of nitrobenzene and methylene chloride was necessary in order to acheive the low temperature required for slow exchange.

Deuteronitromethane was also used as a solvent for the trichloride adduct.

The $CH_3CN.BBr_3$ system was simple in that slow exchange could be acheived using nitrobenzene alone.

For $CH_3CN.BF_3$ a mixed solvent system of deuteronitromethane and dichloromethane was used.

Properties of the Adducts:

Since acetonitrile is a relatively weak Lewis base compared to water, it was necessary to store the adducts in a dry nitrogen atmosphere. In the presence of water the adducts decompose very quickly, the BCl_3 and BBr_3 adducts breaking down to HCl and HBr respectively and yielding a white solid B_2O_3, which has a characteristic absorption at 1260 cm^{-1} in the I.R. region.

The presence of this peak was used as a check on the purity of the adducts.

The BF_3 adduct decomposed in the presence of water, giving off pungent fumes. In an open system, only a trace of water is needed to catalyze the decomposition of this adduct.

Preparation of NMR Samples

All NMR samples were prepared in the nitrogen filled dry box using 5 mm OD NMR capped tubes. The adducts were weighed out into the NMR tube and solvents were added using a Hamilton 2 ml syringe. The excess acetonitrile was added with a 10 microliter capacity Hamilton syringe and the volume checked by weighing, one or two drops of TMS were added, and the capped NMR samples were stored in dry ice if NMR runs could not be performed on the same day.

NMR SPECTRA

The NMR spectra were recorded with a Varian A-60 analytical NMR spectrometer equipped with a V-6040 variable temperature unit which could function from +200° to -150°C with modifications which include a six turn probe insert.

Other accesories included a C 1024 Varian Time Averaging computer and a V-6058A spin decoupler unit. A modification of the sweep zero range adjust to a console mounted helipot was necessary since nitrobenzene solutions had their TMS signals past the upfield end of the normal sweep zero range.

For routine scans, a 500 cps sweep with a 500 sec scan was used. For the more sensitive peak width studies, a 50 cps sweep width with a 500 sec. scan rate gave good results. The exact position of the peaks was found by using audio frequency calibration sidebands produced by a Hewlett Packard 4204A decade oscillator which was double checked with an El Dorado 224 frequency counter.

The temperature of the sample was calibrated with a methanol sample supplied by Varian Associates.

An equation relating the temperature of the sample to the mean difference in peak separation of the methyl and hydroxyl groups was used to calculate the temperature as the Standard Varian curves are in error (42).

The areas of the adduct and free base peak under slow exchange conditions were determined by electronic integration and complemented by weighing the respective traces and/or using a Gelman mechanical planimeter. Since the area of the peak is proportional to the concentration of the species, the ratio of the areas was equal to the ratio of the concentrations.

For activation energy plots, the best straight line was calculated using a least square algol computer program SIXCUR from the G.E. Time Sharing Library. Later, a similar Fortran IV routine written by J.M. Miller for the I.B.M. 360-75 at University of Waterloo (used in linked mode via Brock's I.B.M. 360-20 terminal) was used for fitting the curves.

PURIFICATION OF SOLVENTS

Deuteronitromethane (Diaprep Incorporated) was dried with molecular sieve (4A) before use. Dichloromethane (Eastman organic White Label) was dried with molecular sieve, then distilled, the middle fraction collected at 40°. It was kept over molecular sieve before use. Nitrobenzene (Baker analyzed) was first treated with calcium hydride and then distilled off, the middle portion retained. All the solvents were stored in the dry box.

SPECTRA

I.R. spectra of the solid adducts were recorded as their nujol and hexachlorobutadiene mulls on KBr disks using a Perkin Elmer 237B grating infrared spectrophotometer in the range of 4000 to 625 cm^{-1}. For more sensitive work, the Perkin Elmer 225 grating infrared Spectrophotometer with a wavelength range of 5000 to 200 cm^{-1} was used.

Liquid samples were run in a two stoppered KBr liquid cell down to the KBr cut-off frequencey of 400 cm^{-1}. Ultraviolet and visible spectra of nitrobenzene solutions were run on a Bausch and Lomb 600 and the Cary 14 instruments.

RESULTS

The peak position of the adducts and free acetonitrile under various solvent and temperature conditions are shown in Table 3 Subsequent calculation on the degree of dissociation of the adducts follows. The exchange reactions of the adducts are discussed in detail under their separate sections.

TABLE 3

TABLE OF CHEMICAL SHIFTS OF THE ADDUCTS

Compound	νAB hz	νB hz	Solvent System	Conditions for Observation
$CH_3CN\cdot BBr_3$	191.4	124.5	ϕ-NO_2 neat.	- 1.4°
$CH_3CN\cdot BCl_3$	188.3	124.4	$(\phi NO_2) = 6.09M$	-46.3°
$CH_3CN\cdot BCl_3$	178.5	121.2	Neat CD_3NO_2	-30°
$CH_3CN\cdot BF_3$	162.0	125.5	CD_3NO_2, CH_2Cl_2 $(CD_3NO_2) = 8.09M$	-125

With the NMR probe at ambient temperature (+34°), in neat nitrobenzene, $\nu CH_3CN\cdot BBr_3 = 189.9$

and $\nu CH_3CN\cdot BCl_3 = 182.8$

From a comparison in the peak position for slow exchange, with those at room temperature it is evident that at room temperature, some of the adduct has partially dissociated into its free acid and base producing the upfield shift.

We can use the equation for the single peak position at fast exchange conditions.

$$\nu\text{common} = XAB\,\nu AB + XB\,\nu B$$

to calculate the percent dissociation of the adduct.

For the CH_3CNBBr_3 case,

at room temperature ν obsd = 189.9 hz

νAB = 191.4 hz

νB = 124.5 hz

One obtains $X_B = 2.25 \times 10^{-2}$ therefore at room temperature (34 ^{o}), the adduct is 2.3% dissociated.

Similarily for CH_3CNBCl_3 ,

ν obsd = 182.8

νAB = 188.3

νB = 124.4

and $X_B = 8.6 \times 10^{-2}$

This adduct is 8.6% dissociated. This agrees with the experimental observations that the boron nitrogen bond for BBr_3 is stronger than that of BCl_3 .

It was noted that in general the peak positions were affected as follows:-

1) adding the diluent dichloromethane to a nitrobenzene solution shifted the peaks upfield (increased shielding).
2) increasing the temperature of the sample shifted the peaks upfield.
3) For slow exchange conditions in identical solvent systems, the peak positions of the adduct and free base were independent of concentration.
4) as seen from the CH_3CNBCl_3 system, the adduct in deuteronitromethane experiences a greater upfield shift than for nitrobenzene.

$CH_3CN.BCl_3$

$CH_3CN.BCl_3$ was the first system to be completely studied. A solution of $CH_3CN.BCl_3$ in nitrobenzene was amber whereas neat nitrobenzene is lemon colored. This effect was attributed to:-

1) formation of a weak nitrobenzene - BCl_3 complex and/or
    b) BCl_3 induced decomposition of the solvent. (17)

Brown and Holmes (17) have isolated the nitrobenzene boron trichloride and the tribromide complexes as reddish colored solids which decompose readily when exposed to the atmosphere.

Visible spectra of nitrobenzene boron trichloride in nitrobenzene were run and two peaks were observed at 425 mu and 490 mu. Unfortunately, nitrobenzene absorbs strongly around 425 mu and therefore quantitative results for the nitrobenzene boron trichloride complex could not be obtained.

The peak at 490 mu is indicative of solvent decomposition since its intensity increased after the solution was left standing for several days. This intensity increase was accompanied by a gradual darkening of the solvent.

Slow irreversible hydrolysis of the adduct in solution was also occuring as evidenced by the formation of a solid gell substance in the sample tubes which did not redissolve upon heating of the solution.

In fact when the NMR solutions adducts were made up, there was often some initial hydrolysis of the adduct. This had to be corrected for in the calculation of concentrations of species present.

When excess acetonitrile was added to an acetonitrile boron trichloride solution in nitrobenzene, only a single NMR peak was observed and the position of the peak lay between that of free acetonitrile and the adduct. This, as was pointed out previously, is indicative of a fast exchange reaction.

Cooling of the NMR samples to obtain slow exchange conditions was achieved with a nitrobenzene- dichloromethane solvent in which the volume ratio was 1:1.19.

The main resonance and satellite peaks due to the solvents were well outside the range of interest.

Using this solvent mixture, several samples were made up of adduct with excess acetonitrile of varying concentration of adduct and acetonitrile.

Spectra were observed in the slow exchange region (-33 to -55) where particular rate equations apply. As was mentioned previously, concentration of adduct and acetonitrile were calculated from the relative areas of the peaks and the initial concentration of adduct and acetonitrile was corrected for the slight hydrolysis of the adduct as well as its dissociation at that temperature. The mechanism for exchange was deduced from line broadening data and is tabulated in the following Tables: 2,3 and 4.

Typical NMR spectra in the slow and fast exchange regions is also shown in Figure 2.

FIGURE 2

TYPICAL NMR SPECTRA OF $CH_3CN \cdot BCl_3$ - CH_3CN

IN

NITROBENZENE, DICHLOROMETHANE FOR

SLOW AND FAST EXCHANGE

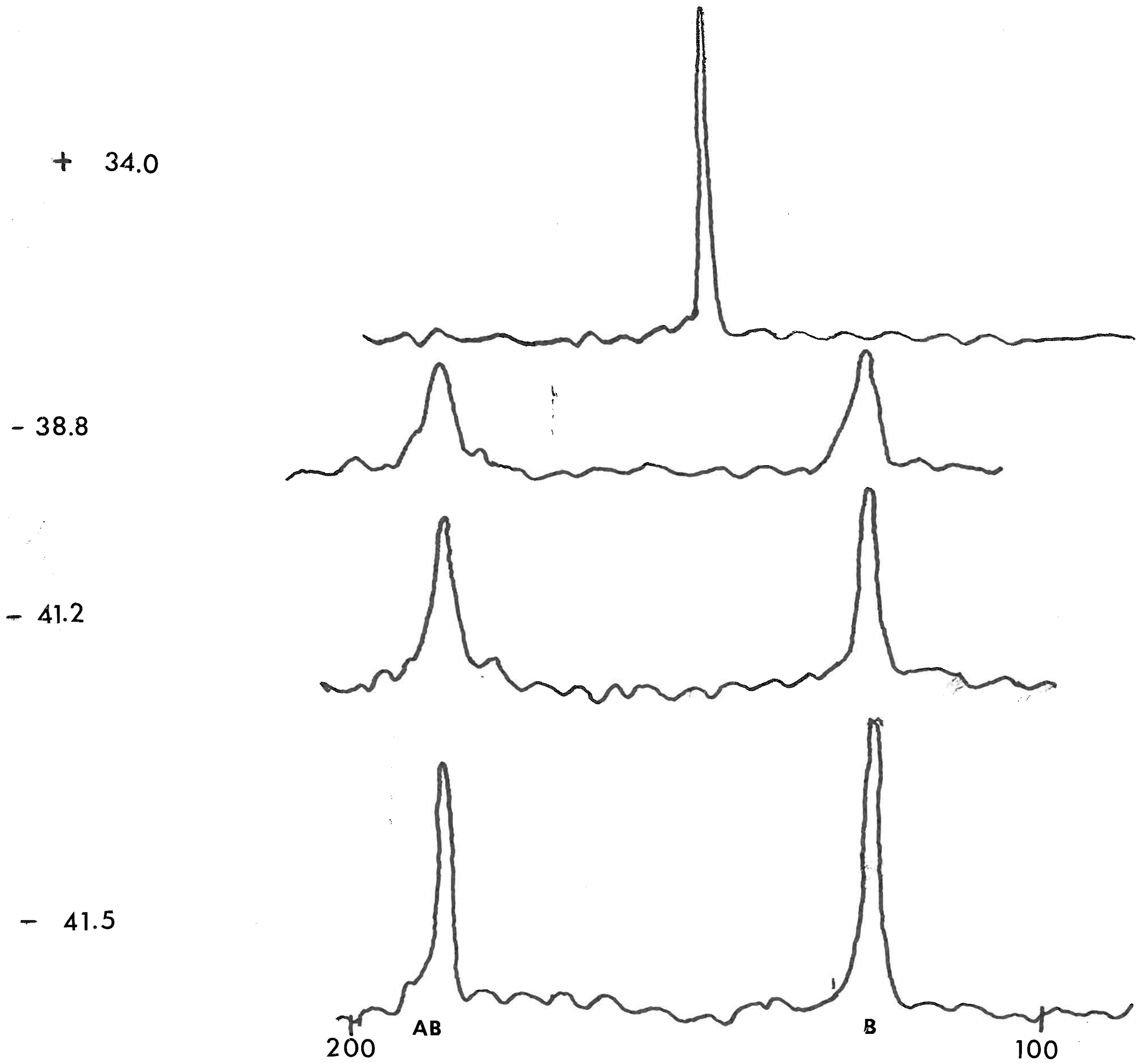

+ 34.0
- 38.8
- 41.2
- 41.5
AB
B
200
100

TABLE 2

Evaluation of $\frac{1}{T_{AB}}$ and $\frac{1}{T_B}$ Values For CH_3CNBCl_3-CH_3CN in ϕNO_2, CH_2Cl_2 at -38.9°

Soln No.	Δ_{AB} hz	Δ^{o} hz	$(\Delta_{AB} - \Delta o)$	$\frac{1}{T_{AB}}$ sec^{-1}	Δ B	$(\Delta B - \Delta o)$	$\frac{1}{T_B}$ sec^{-1}
(1)	2.50	0.45	2.05	7.45	0.85	0.40	1.25
(2)	2.59	0.45	2.14	6.50	1.20	0.75	2.36
(3)	2.58	0.45	2.13	6.69	1.84	1.39	4.37
(4)	2.52	0.45	2.07	6.72	2.05	1.60	5.03
(5)	2.82	0.45	2.37	6.44	5.72	5.27	16.6

Δ AB = full peak width at half height

Δ^{o} = TMS width at half height

TABLE 3

MECHANISM OF CH_3CNBCl_3-CH_3CN EXCHANGE IN NITROBENZENE, DICHLOROMETHANE

No.	(AB) x 10^2 M	(B) x 10^2 M	$\frac{1}{T_{AB}}$ sec^{-1}	$\frac{1}{T_B}$ Sec^{-1}	(AB)/ (B)	$\frac{1}{T_B / \frac{(AB)}{(B)}}$ sec^{-1} M^{-1}
1	4.10	13.8	7.45	1.26	0.298	4.22
2	4.63	10.5	6.50	2.36	0.441	5.34
3	6.04	7.29	6.69	4.37	0.827	5.28
4	5.85	4.79	6.72	5.03	1.222	4.11
5	6.78	3.53	6.44	16.56	1.921	8.62
		Average	6.59 ± 0.15			4.73 ± 0.61

TABLE 4

FURTHER MECHANISTIC STUDIES ON THE SAME SYSTEM

-34.2°				-42.7°		
$\frac{(AB)}{(B)}$	$\frac{1}{T_{AB}}$ sec^{-1}	$\frac{1}{T_B}$ sec^{-1}	$\frac{1}{T_B}/\frac{(AB)}{(B)}$ sec^{-1} M^{-1}	$\frac{1}{T_{AB}}$ sec^{-1}	$\frac{1}{T_B}$ sec^{-1}	$\frac{1}{T_B}/\frac{(AB)}{(B)}$ sec^{-1} M^{-1}
0.298	11.22	2.95	9.91	3.93	0.53	1.79
0.441	11.78	4.65	10.55	3.52	1.38	3.13
0.827	10.74	7.76	9.38	3.49	2.83	3.42
1.222	9.58	13.98	11.44	3.99	5.25	4.29
1.921	13.67	24.66	12.84	3.90	6.38	3.32
AVERAGE	11.4 ±2.3		10.8 ± 2.0	3.77± 0.25		3.29 ± 1.0

As seen in Tables 2,3 and 4, the value of $\frac{1}{T_{AB}}$ within experimental error is independent of concentration terms and equal to the rate constant of dissociation and $\frac{1}{T_B} = \frac{1}{T_{AB}} \frac{(AB)}{(B)}$.

This is consistent with a dissociation exchange of CH_3CNBCl_3 in this mixed solvent.

$E^{\ddagger}$ was calculated from the Arrhenius plots as shown in figures 3 and 4, the parameters plotted being obtained from Table 5.

TABLE 5

EVALUATION OF ACTIVATION ENERGIES FOR $CH_3CN{\cdot}BCl_3$ - CH_3CN EXCHANGE

Temp °C	$\frac{1}{T} \times 10^3$ (degk)$^{-1}$	$\frac{1}{T_{AB}}$ sec^{-1}	ln $\frac{1}{T_{AB}}$	$\frac{1}{T_B}$ sec^{-1}	ln $\frac{1}{T_B}$
-35.7	4.211	9.11	2.21	7.73	2.05
-38.8	4.266	8.23	2.11	7.13	1.97
-41.2	4.310	5.15	1.64	5.09	1.63
-42.8	4.340	4.81	1.57	4.08	1.41
45.5	4.393	2.89	1.06	2.07	0.73
-47.7	4.436	-	-	1.70	0.53

For ln $\frac{1}{T_{AB}}$ vs $\frac{1}{T}$ E = 12.83 ± 0.50 Kcal/mole

For ln $\frac{1}{T_B}$ vs $\frac{1}{T}$ E = 13.22 ± 0.50 Kcal/mole

Average value of $E^{\ddagger}$ E = 13.0 Kcal/mole

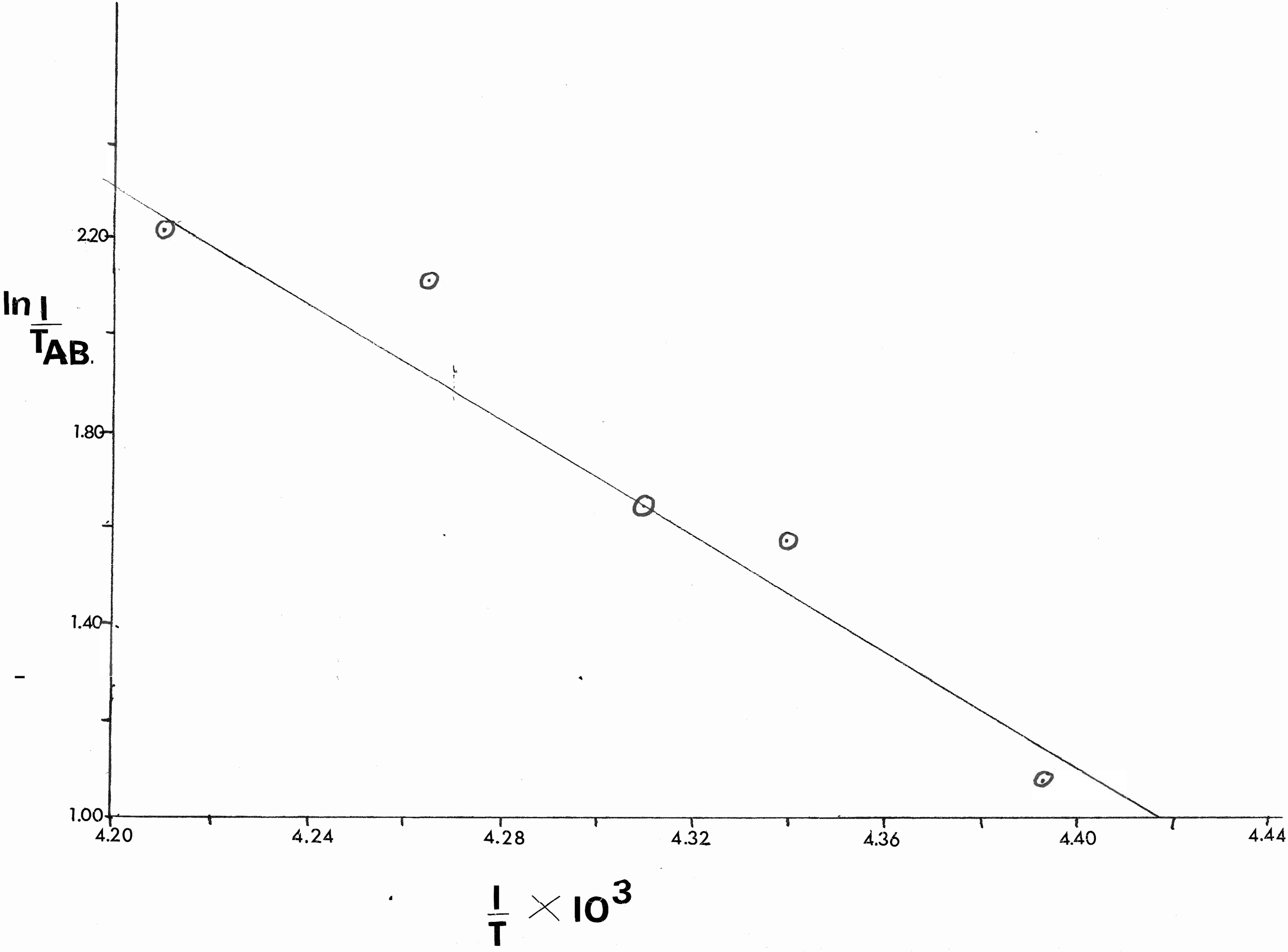
FIGURE 3

EVALUATION OF ACTIVATION ENERGY FOR $CH_3CN.BCl_3$ - CH_3CN EXCHANGE

IN

NITROBENZENE, DICHLOROMETHANE MIXED SOLVENT IN VOLUME RATIO 1:1.19

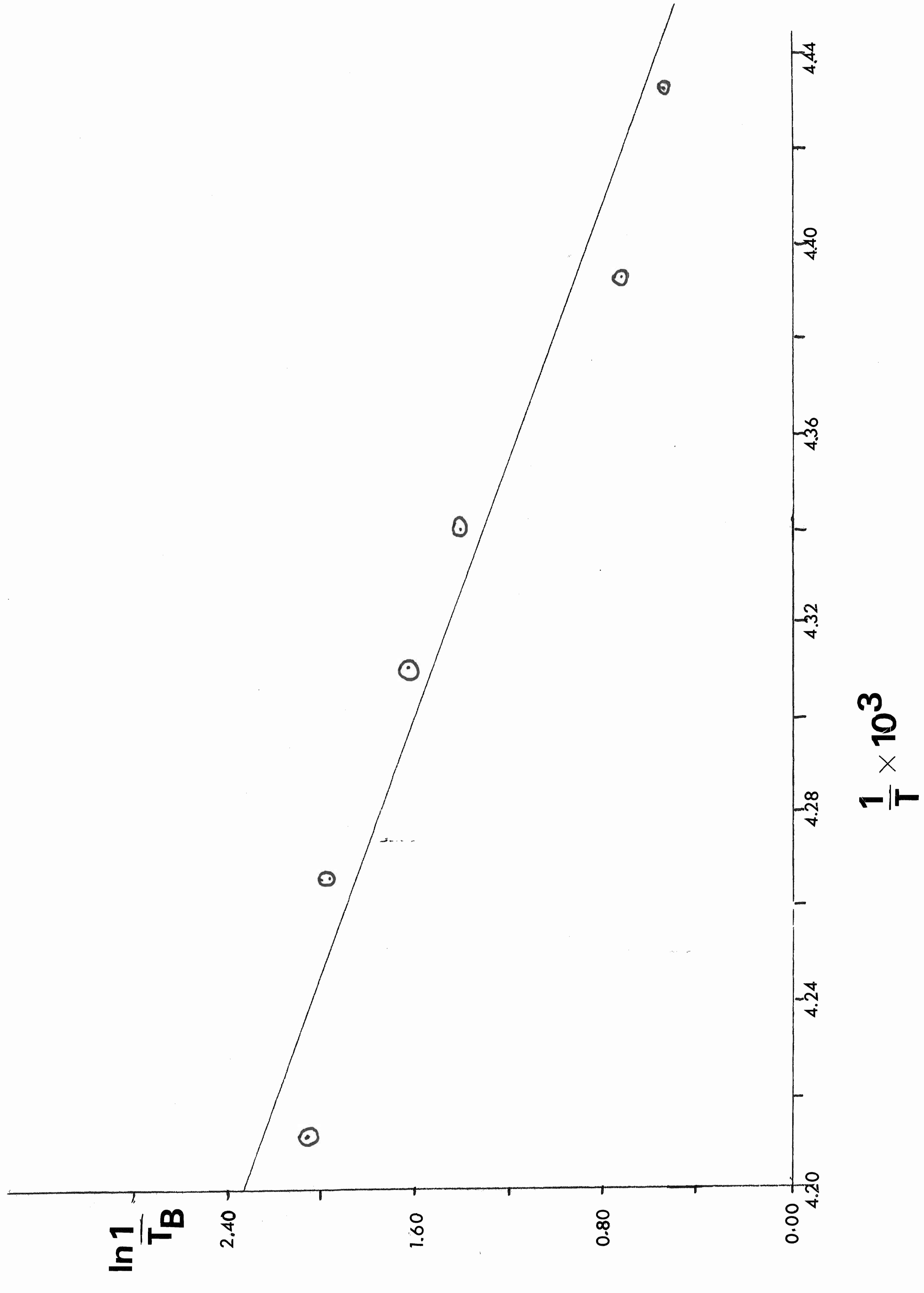
FROM ADDUCT PEAK BROADENING



ln 1/T_AB.
2.20
1.80
1.40
1.00
4.20
4.24
4.28
4.32
4.36
4.40
4.44
1/T × 10^3

FIGURE 4

Activation Energy For $CH_3CN{\cdot}BCl_3$ - CH_3CN Exchange On Same System From Free Acetonitrile Peak Broadening



$\ln \frac{1}{T_B}$
2.40
1.60
0.80
0.00
4.20
4.24
4.28
4.32
4.36
4.40
4.44
$\frac{1}{T} \times 10^3$

The activation energy was also evaluated from other independent samples of adduct and free base using the same solvent ratio. The results obtained for another sample are shown in Table 6 and Figures; 5 and 6.

Values of 12.30 and 12.42 Kcal mole^{-1} were obtained. The averaged value is 12.36 ± 0.6 Kcal mole^{-1}.

TABLE 6

Activation Energy for $CH_3CN.BCl_3$ - CH_3CN Exchange Using Similar Solvent Conditions

Temp °C	$\frac{1}{T} \times 10^3$	$\frac{1}{T_{AB}}$ sec^{-1}	$\ln \frac{1}{T_{AB}}$	$\frac{1}{T_B}$ sec^{-1}	$\ln \frac{1}{T_B}$ sec^{-1}
-51.3	4.507	1.602	0.4713	0.848	0.165
-47.5	4.431	2.136	0.7589	1.445	0.368
-44.8	4.378	2.827	1.039	1.979	0.683
-42.7	4.338	3.487	1.249	3.204	1.164
-40.1	4.290	5.372	1.681	3.519	1.258
-38.9	4.268	6.566	1.882	4.084	1.407
-35.8	4.212	8.954	2.192	7.068	1.956
-34.2	4.184	11.41	2.434	7.760	2.049

E_{AB} = 12.42 ± 0.40 Kcal/mole E_B = 12.30 ± 0.40 Kcal/mole

FIGURE 5

ACTIVATION ENERGY FOR CH_3CNBCl_3 - CH_3CN IN NITROBENZENE, DICHLOROMETHANE IN VOLUME RATIO 1:1.19 FROM ADDUCT PEAK BROADENING

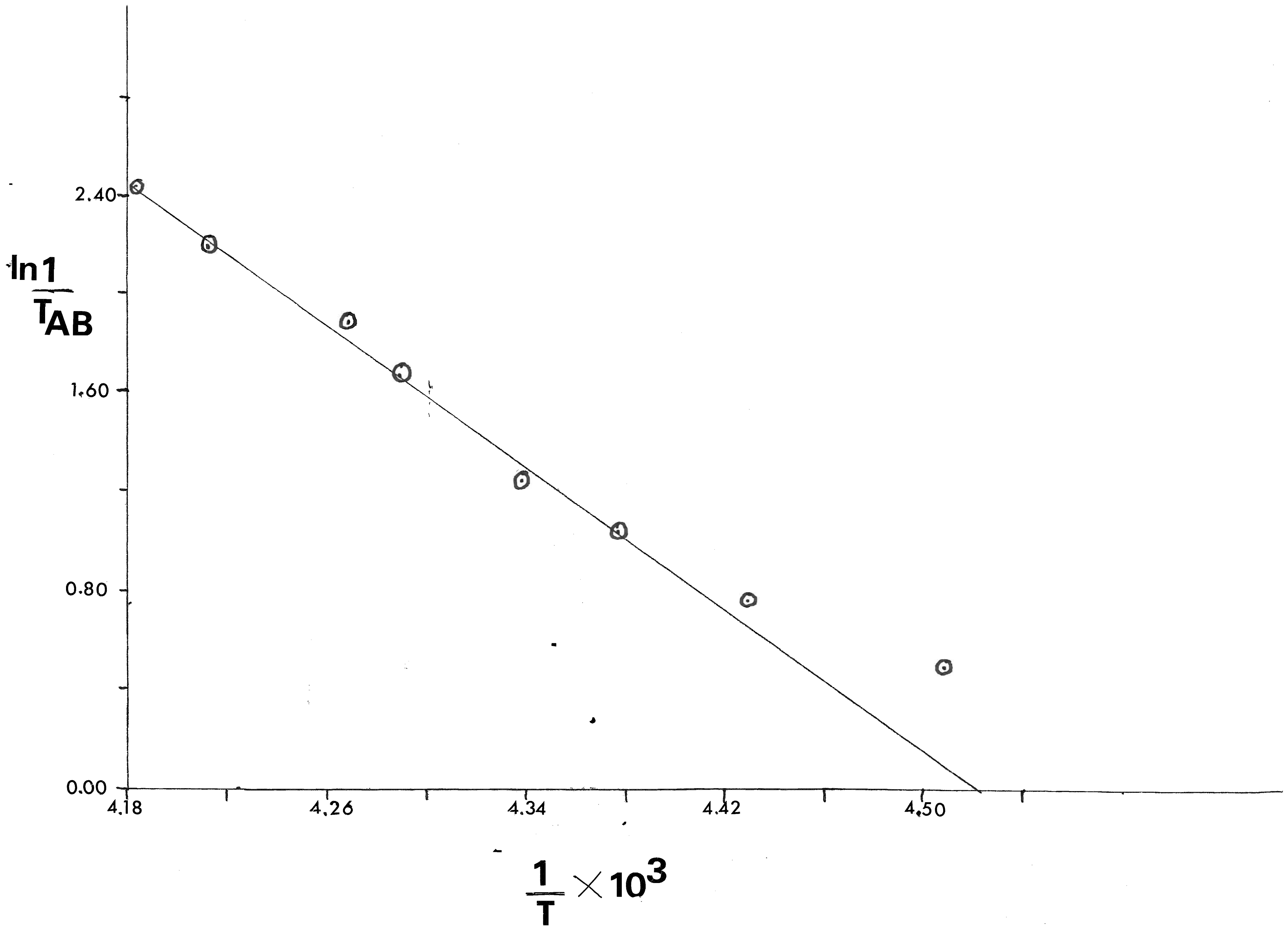
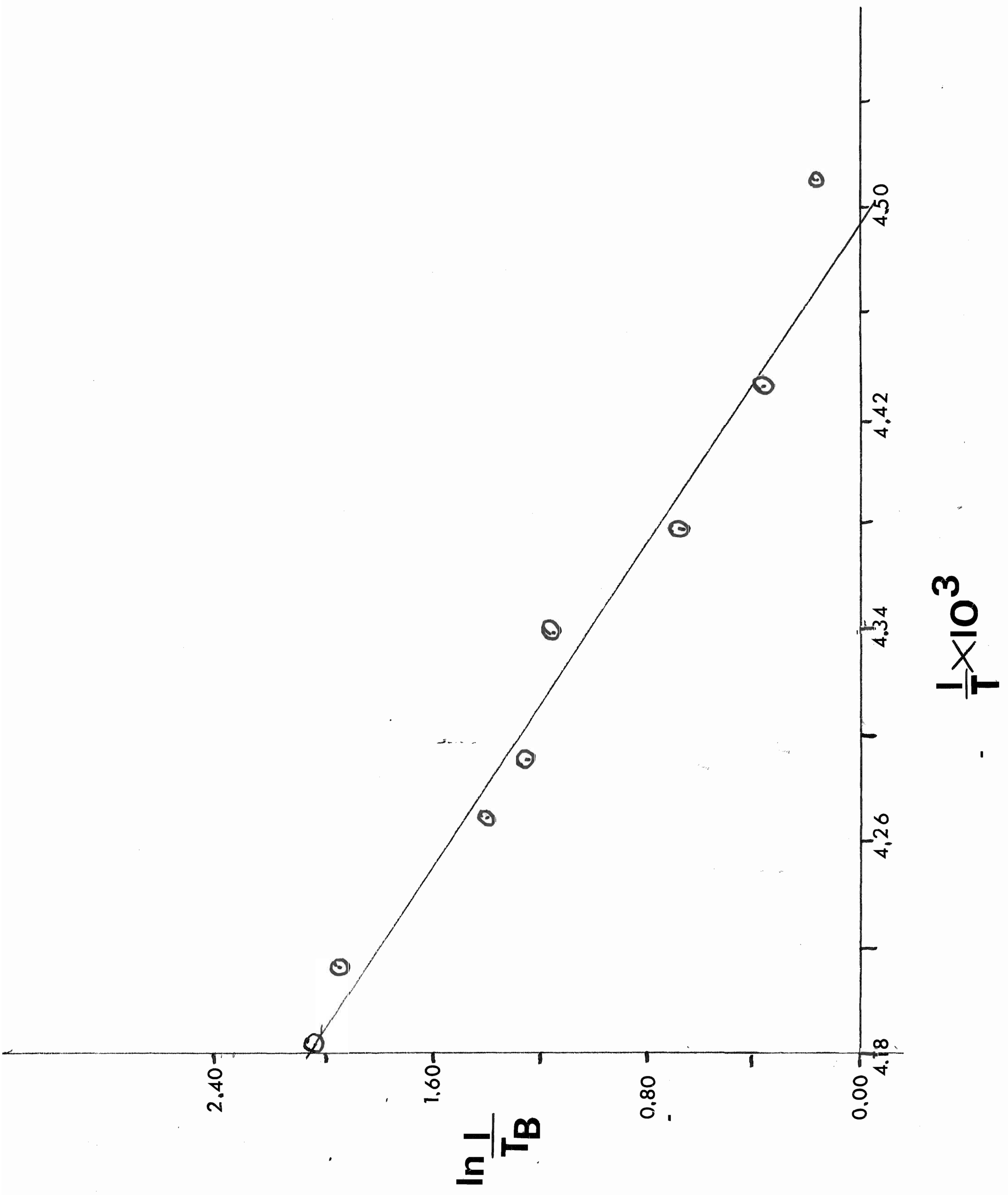

ln 1/T_AB
2.40
1.60
0.80
0.00
4.18
4.26
4.34
4.42
4.50
1/T × 10^3

FIGURE 6

ACTIVATION ENERGY FOR CH_3CNBCl_3 - CH_3CN EXCHANGE FROM ACETONITRILE PEAK BROADENING


2.40
1.60
0.80
0.00
4.18
4.26
4.34
4.42
4.50
ln 1/T_B
1/T ×10^3

The average value for the activation energy for this solvent system is 12.8 ± 0.4 Kcal.

Calculations by Lockhart and Blackborow(23) indicate that in solution the dissociation energy of the B-N bond in $CH_3CN.BCl_3$ is 18.1 Kcal.

Our depressed value of 12.8 Kcal for dissociation led us to suspect that nitrobenzene was participating in the dissociation by lowering the energy for exchange in the formation of some sort of weak intermediate nitrobenzene boron trichloride complex. In fact, Brown and Holmes have calculated an adduct strength of 8.7 ± 0.2 Kcal for the nitrobenzene boron trichloride complex.

It was decided to vary the concentration of nitrobenzene in the mixed solvent to see whether any dependence of the activation energy on the composition of the solvent mixture existed.

The following data was obtained as seen in Table 7 and shown as a plot in Figure 7.

TABLE 7

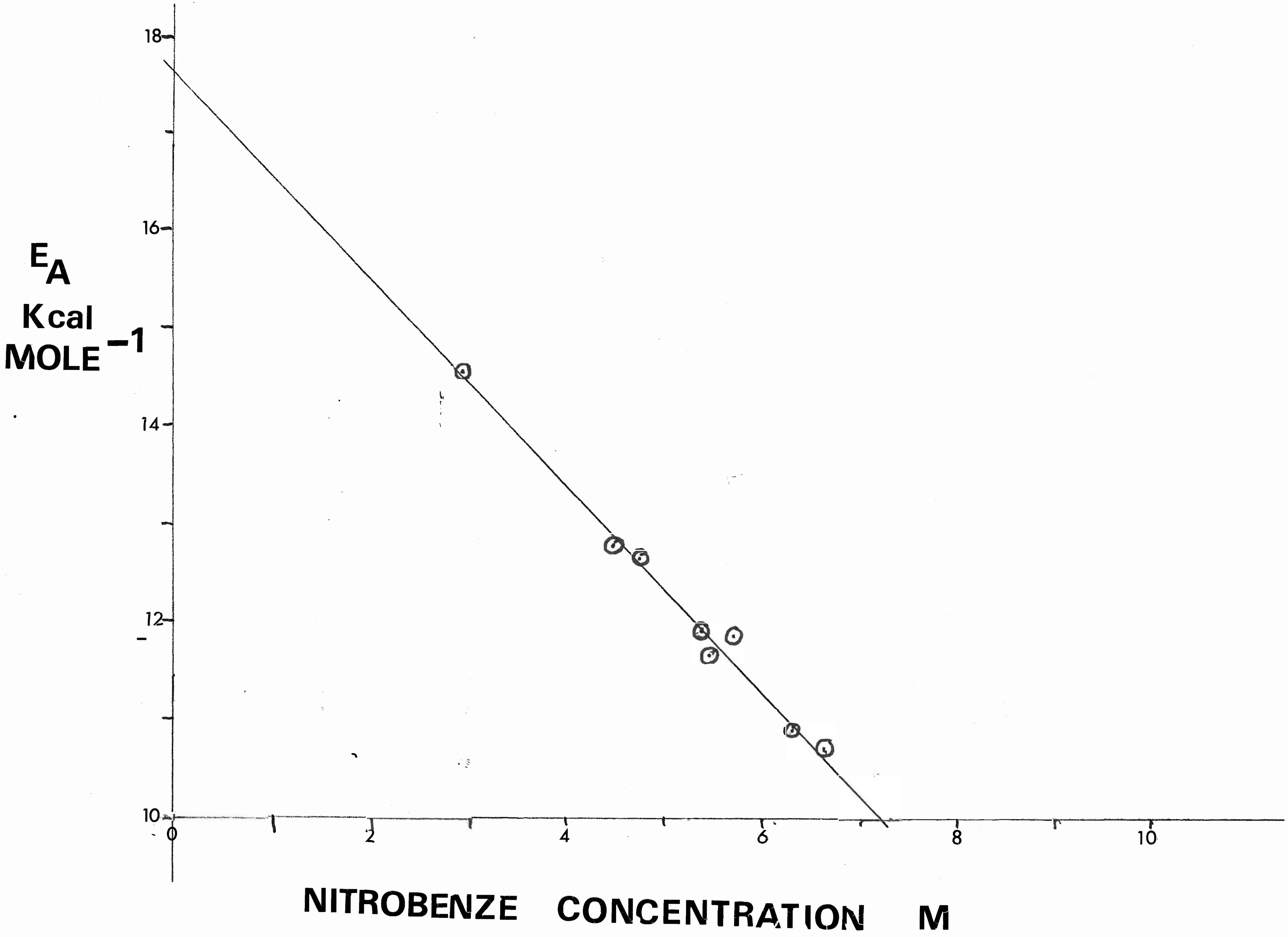
Effect of Nitrobenzene Concentration on Activation Energy for $CH_3CN.BCl_3$ - CH_3CN Exchange

E_A Kcal mole^{-1}	$(\phi\text{-}NO_2)\frac{20^oC}{M}$
10.7 ± 0.4	6.630
10.9 ± 2.0	6.300
11.7 ± 0.2	5.482
11.9 ± 0.9	5.348
12.7 ± 0.7	4.757
12.8 ± 0.3	4.453
14.6 ± 1.3	2.956
11.9 ± 1.8	5.743

FIGURE 7

Effect of Nitrobenzene Concentration on Activation Energy For

$CH_3CN{\cdot}BCl_3$ -CH_3CN Exchange


E_A
Kcal
MOLE $^{-1}$
18
16
14
12
10
0
2
4
6
8
10
NITROBENZE CONCENTRATION M

The plot of E vs (ϕNO_2) extrapolated to zero nitrobenzene concentration (Figure 7) yields an activation energy of 17.65 Kcal. The extrapolated value for neat nitrobenzene (9.737M) is 7.17 Kcal.

The value of 17.65 for the CH_2Cl_2 extrapolation (inert solvent) agrees very well with the Lockhart & Blackborow value of 18.1).

From the same studies, the variation of $\frac{1}{T_{AB}}$ with solvent concentration was also observed. The values obtained are tabulated in Table 8.

TABLE 8

Variation of $\frac{1}{T_{AB}}$ $(\frac{1}{T_{AB}} = k)$ With Nitrobenzene Concentration

at

-37.1°	
$\frac{1}{T_{AB}}$ hz	(ϕNO_2) M
6.57	6.63
9.17	5.35
12.72	4.76
12.85	4.38

-46.3	
$\frac{1}{T_{AB}}$ hz	(ϕNO_2) M
2.42	6.63
2.77	5.35
3.42	4.76
3.36	4.38

-44.8	
$\frac{1}{T_{AB}}$ hz	(ϕNO_2) M
3.14	6.63
4.68	5.35
4.78	4.76
5.45	4.38

-42.2	
$\frac{1}{T_{AB}}$ hz	(ϕNO_2) M
3.86	6.63
5.12	5.35
6.25	4.76
6.50	4.38

The values from Table 8 show that as the nitrobenzene concentration is increased, the rate constant for exchange decreases. The significance of this observation will be discussed in the next section.

Deuteronitromethane was also used as a solvent for the CH_3CNBCl_3, CH_3CN system. Unlike the mixed solvent system, slow exchange conditions were achieved at higher temperatures (-35 to -17) i.e.- at given temperature, the rate of exchange in deuteronitromethane is slower than in the mixed solvent. Variable concentration and variable temperature studies were also performed on this system.

The data as shown in Tables 9 and 10 prove that dissociation is the pathway for exchange.

TABLE 9

Concentration Studies on $\frac{1}{T}$ values for CH_3CNBCl_3, CH_3CN in CD_3NO_2.

at -24.5°

(AB) x10^2 Molar	(B) x10^2 Molar	$\frac{1}{T_{AB}}$ sec^{-1}	$\frac{1}{T_B}$ sec^{-1}	$\frac{(AB)}{(B)}$	$\frac{1}{T_B}$ / $\frac{(AB)}{(B)}$ sec^{-1}
8.19	7.75	9.11	5.45	1.057	5.16
7.15	13.52	8.29	3.07	0.529	5.80
13.51	39.9	9.86	1.82	0.339	5.37
10.59	60.9	9.30	1.38	0.174	7.93
	AVERAGE	9.14 ± 0.72			Average 5.44 ± 0.36

TABLE 10

FURTHER CONCENTRATION STUDIES ON THE $CH_3CN{\cdot}BCl_3$-CH_3CN SYSTEM IN CD_3NO_2

-28.2°

(AB) x 10^2 M	(B) x 10^2 M	$\frac{1}{T_{AB}}$ sec^{-1}	$\frac{1}{T_B}$ sec^{-1}	$\frac{(AB)}{(B)}$	$\frac{1}{T_B}$ / $\frac{(AB)}{(B)}$ sec^{-1}
8.19	7.75	5.53	15.90	1.057	15.0
7.15	13.5	5.06	8.29	0.529	15.7
13.5	39.9	5.56	4.40	0.339	13.0
10.6	60.9	5.75	2.83	0.174	16.3
	Average	5.47 ±	0.41	Average	15.0 ± 2.0

-19.4°

8.19	7.75	11.22	18.28	1.057	17.3
7.15	13.5	13.04	11.22	0.529	21.2
13.5	39.9	14.89	7.19	0.339	21.2
10.6	60.9	12.50	4.02	0.174	23.1
Average		12.91 ±	1.98		21.2

In this series of experiments, the errors inherent in the calculation of (AB)/(B) from the area of the peaks accounts for the deviation of $\frac{1}{T_B}/\frac{(AB)}{(B)}$ for the $\frac{1}{T_{AB}}$ value in Tables 9 and 10.

From many samples of CH_3CNBCl_3 in this solvent system, the activation energy for exchange was obtained from the values of the adduct peak broadening. Table 11 and Figure 8 show the results of this plot.

Solvent participation occurs in this system but to a lesser extent than in nitrobenzene solution.

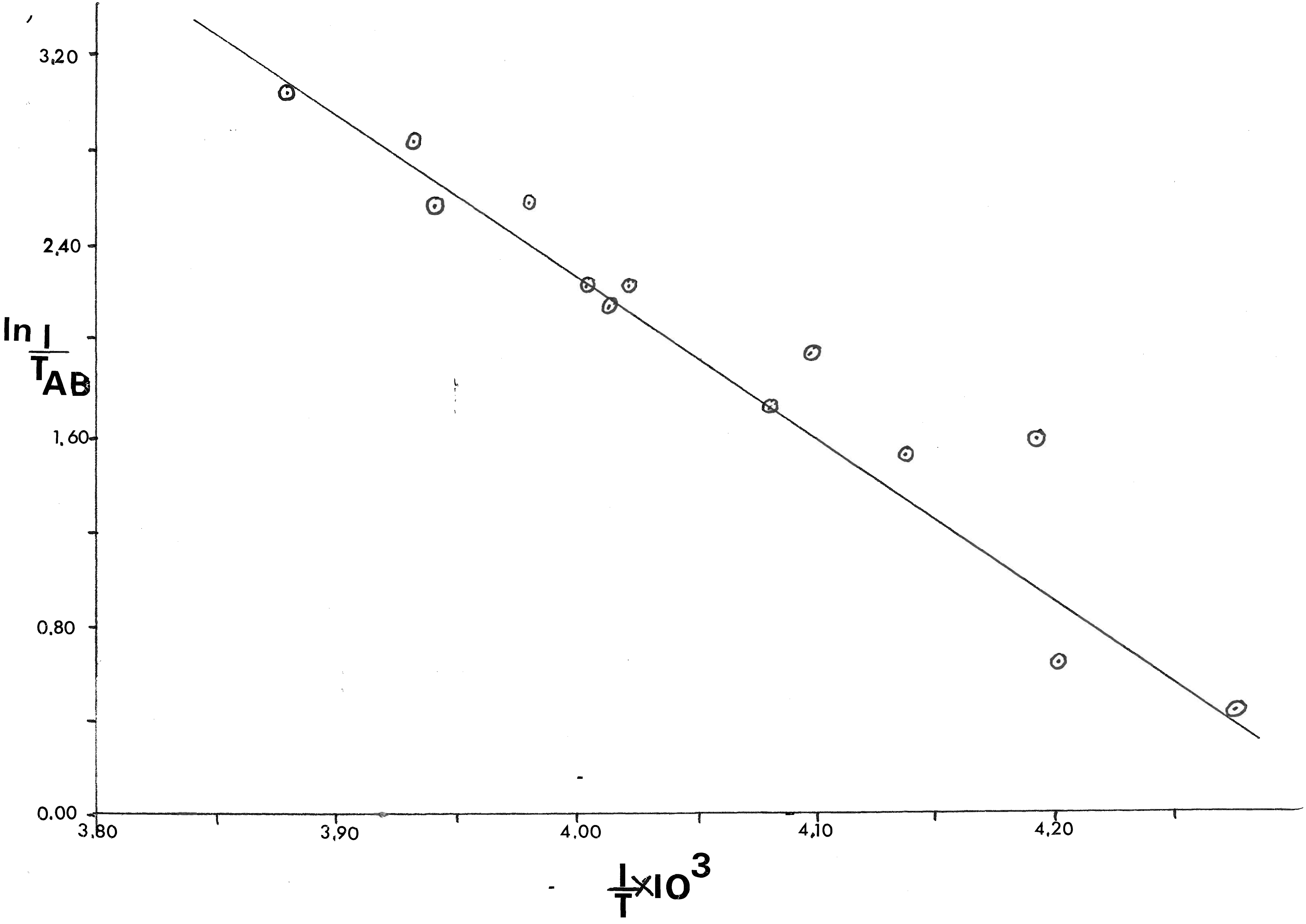
TABLE 11

Calculation of Activation Energy For $CH_3CN \cdot BCl_3$, CH_3CN in CD_3NO_2 Using $\frac{1}{T_{AB}}$ Values

$\frac{1}{T} \times 10^3$	$\ln \frac{1}{T_{AB}}$
4.275	0.4311
4.201	0.6173
4.194	1.567
4.138	1.488
4.098	1.933
4.082	1.699
4.022	2.212
4.014	2.131
4.005	2.216
3.982	2.579
3.941	2.558
3.933	2.822
3.881	3.027

Figure 8

Activation Energy for $CH_3CN{\cdot}BCl_3$-CH_3CN Exchange in CD_3NO_2


3,20
2,40
1,60
0,80
0,00
ln 1/T_AB
3,80
3,90
4,00
4,10
4,20
1/T×10³

CH_3CNBBr_3

Unlike the $CH_3CN.BCl_3$ adducts, slow exchange conditions were attained in neat nitrobenzene in the temperature range of -5° to + 25°.

Variable concentration studies were performed to determine the mechanism. The data obtained (Tables12 and 13) shows definitely that exchange occurs via dissociation of the adduct.

Figure 9 shows typical spectra for $CH_3CN.BBr_3$ exchanging systems.

Figure 9

Typical Spectra for $CH_3CN{\cdot}BBr_3$ - CH_3CN system in Nitrobenzene.

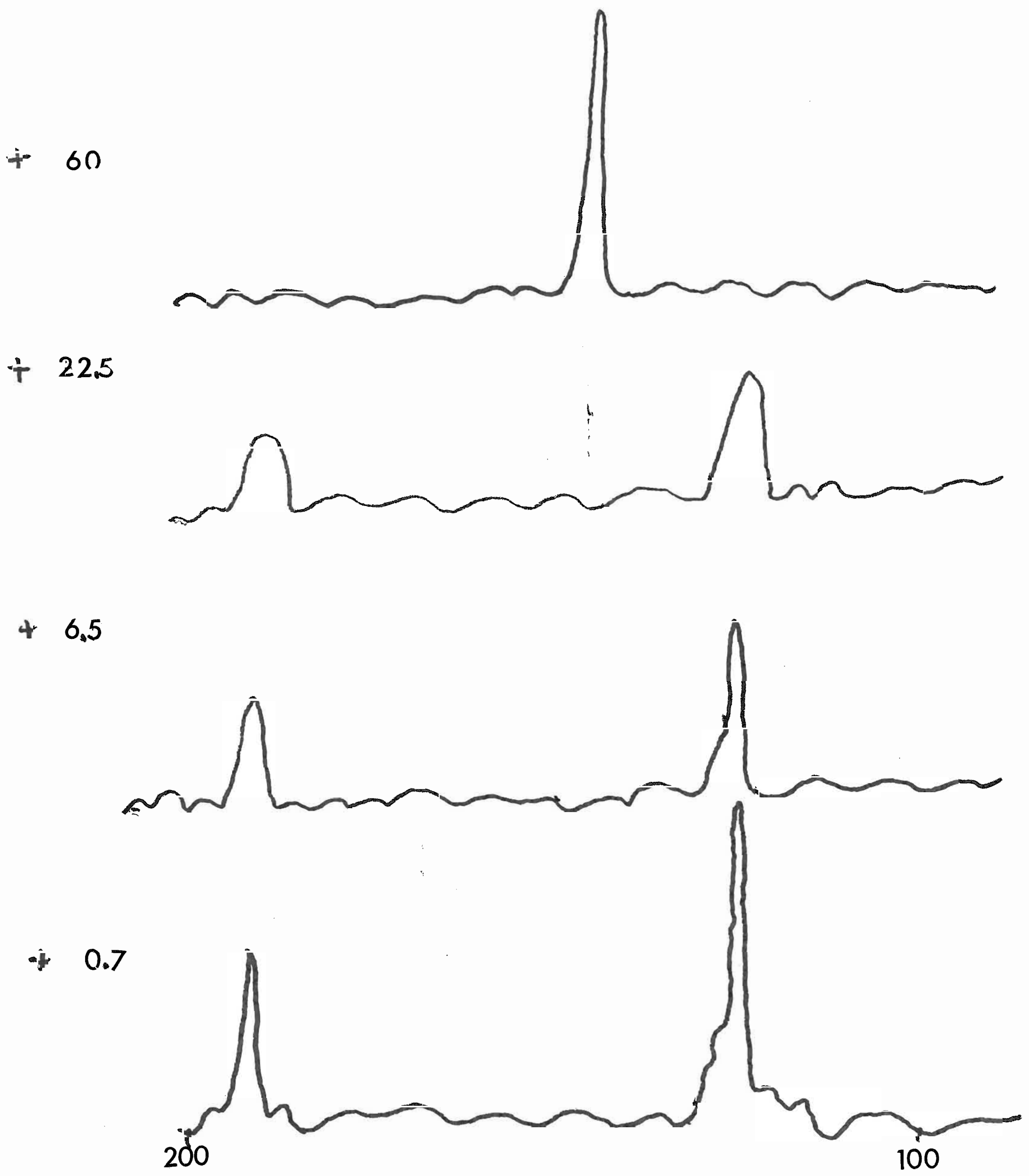

60
22.5
6.5
0.7
200
100

TABLE 12

Variable Concentration Studies of Effect on $\frac{1}{T_{AB}}$ and $\frac{1}{T_B}$ for

for $CH_3CN{\cdot}BBr_3$ - CH_3CN in Neat Nitrobenzene

	(AB) x 10^2 M	(B) x 10^2 M	$\frac{1}{T_{AB}}$ sec^{-1}	$\frac{1}{T_B}$ sec^{-1}	$\frac{(AB)}{(B)}$	$\frac{1}{T_B}$ / $\frac{(AB)}{(B)}$ sec^{-1} M^{-1}
-1.4°c	5.45	5.59	2.890	1.728	0.975	1.77
	3.14	4.91	2.890	1.445	0.639	4.52
	4.70	14.1	2.985	0.754	0.333	2.26
	1.42	12.9	2.733	-	0.110	
	1.57	21.3	2.356	-	0.0739	
	Average		2.890		Average	2.85 ± 1.67
+ 5.5°	5.45	5.59	3.739	2.10	0.975	2.24
	3.14	4.91	4.053	1.89	0.639	2.95
	4.70	14.1	4.273	1.24	0.333	3.73
	1.42	12.9	4.807	-	0.110	-
	1.57	21.3	3.958	-	0.0739	-
	Average		4.17 ± 0.43		Average	2.97 ± 0.76

TABLE 13

Mechanism for $CH_3CN.BBr_3$- CH_3CN Exchange in Neat Nitrobenzene.

	(AB) x 10^2 M	(B) x 10^2 M	$\frac{1}{T_{AB}}$ sec^{-1}	$\frac{1}{T_B}$ sec^{-1}	$\frac{(AB)}{(B)}$	$\frac{1}{T_B}$ / $\frac{(AB)}{(B)}$ sec^{-1}
9.3°	5.45	5.59	5.53	5.40	0.975	5.54
	3.14	4.91	6.50	3.17	0.639	4.97
	4.70	14.1	5.47	1.73	0.333	5.24
		Average	5.83		Average	5.25
			± 0.67			± 0.28
+20.7°	5.45	5.59	12.22	12.38	0.975	12.70
	3.14	4.91	10.21	9.58	0.639	15.00
	4.70	14.1	14.11	4.27	0.333	12.83
		Average	12.18			12.76
			± 1.93			± 0.07

The data for the Activation Energy is calculated for this dissociation process as are shown in Table 14 and Figures 10 and 11 and from Table 15.

TABLE 14

Activation Energy for $CH_3CN{\cdot}BBr_3$, CH_3CN in neat nitrobenzene from $\frac{1}{T}$ values.

t °C	$\ln \frac{1}{T_{AB}}$	$\frac{1}{T} \times 10^3$	$\ln \frac{1}{T_B}$
20.7	2.65	3.40	1.45
13.7	2.23	3.49	0.729
9.3	1.70	3.54	0.547
5.5	1.45	3.59	0.216
- 1.4	1.09	3.68	- 0.282

From $\frac{1}{T_{AB}}$ values, E_{AB} = 11.6 ± 0.90 Kcal/mole

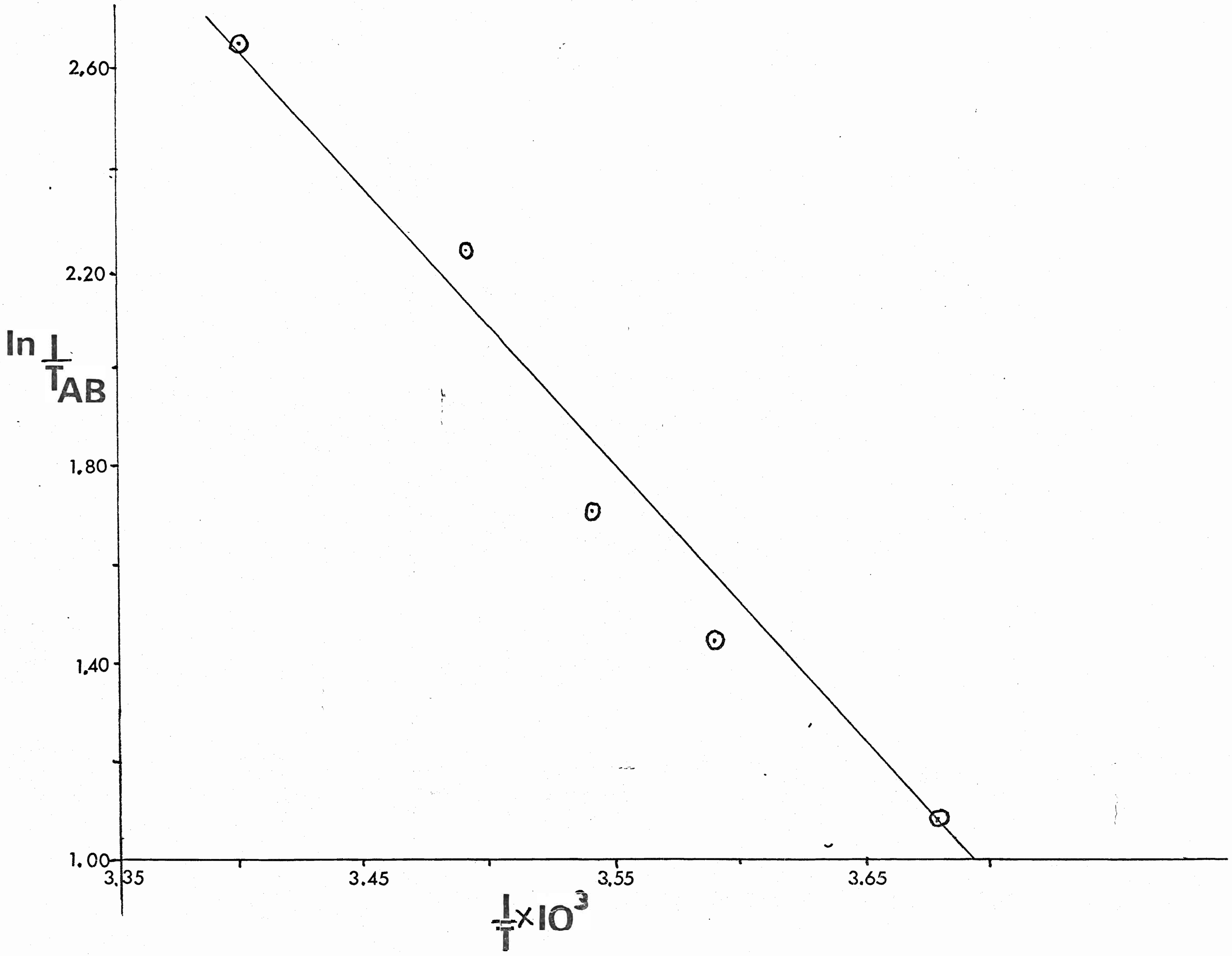
From $\frac{1}{T_B}$ values E_B = 12.1 ± 0.40 Kcal/mole

E Average = 11.9 ± 0.3 Kcal

Figure 10

Activation Energy for $CH_3CN{\cdot}BBr_3$-CH_3CN

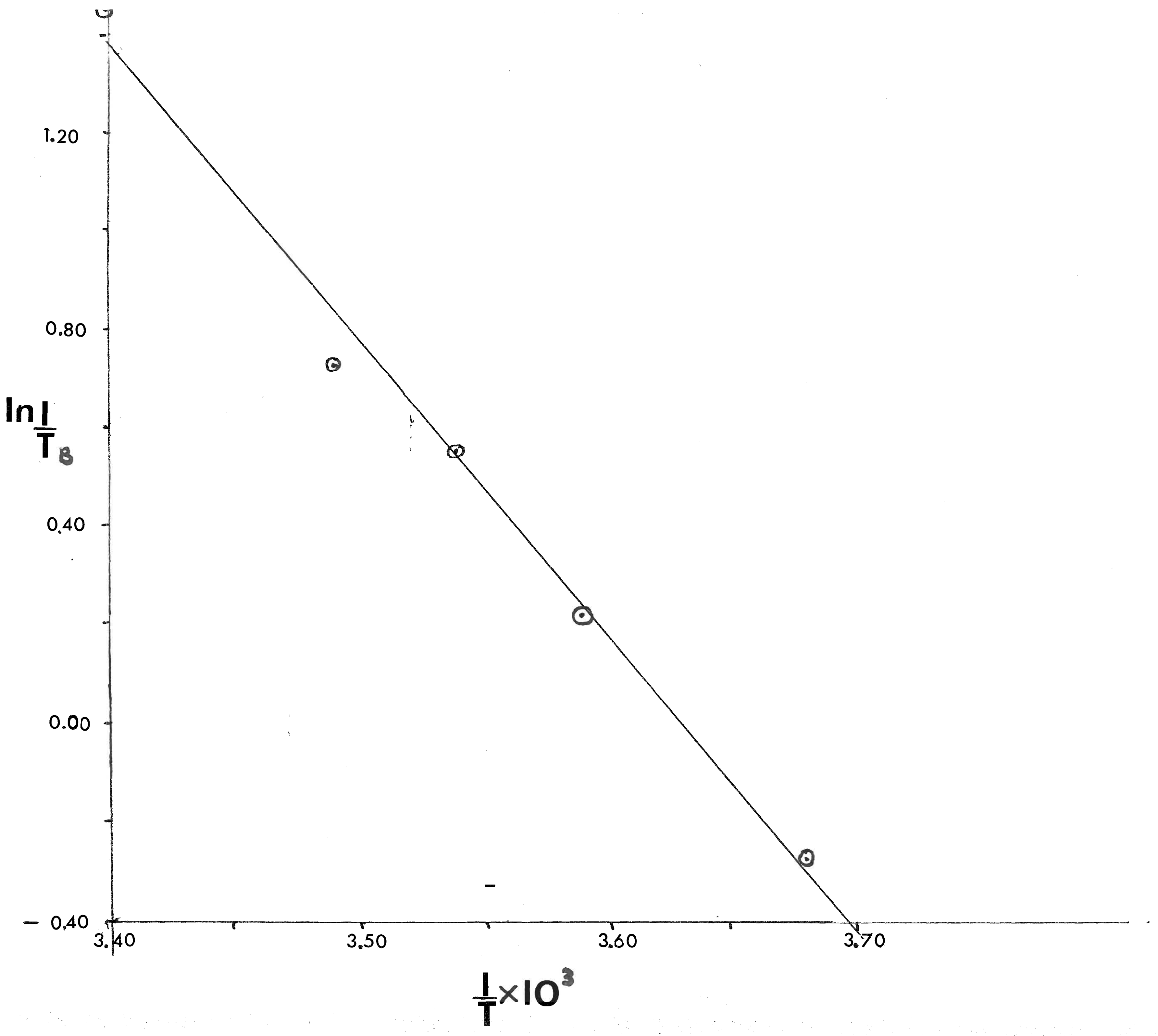
Exchange as Calculated from the Adduct peak



2.60
2.20
$\ln \frac{1}{T_{AB}}$
1.80
1.40
1.00
3.35
3.45
3.55
3.65
$\frac{1}{T} \times 10^3$

Figure 11

Activation Energy for CH_3CNBBr_3-CH_3CN Exchange as calculated from the free base.


1.20
0.80
0.40
0.00
− 0.40
$\ln \frac{1}{T_B}$
3.40
3.50
3.60
3.70
$\frac{1}{T} \times 10^3$

Blackborow and Lockhart have calculated a value of 19.1 Kcal for the dissociation energy of the BBr_3 adduct. Our value of 11.9 Kcal was again too low and solvent effects were evident. A study of the effects of additions of the inert diluent dichloromethane on the activation energy was undertaken. The results obtained are given in Table 15 and the graph illustrated in Figure 12.

Table 15

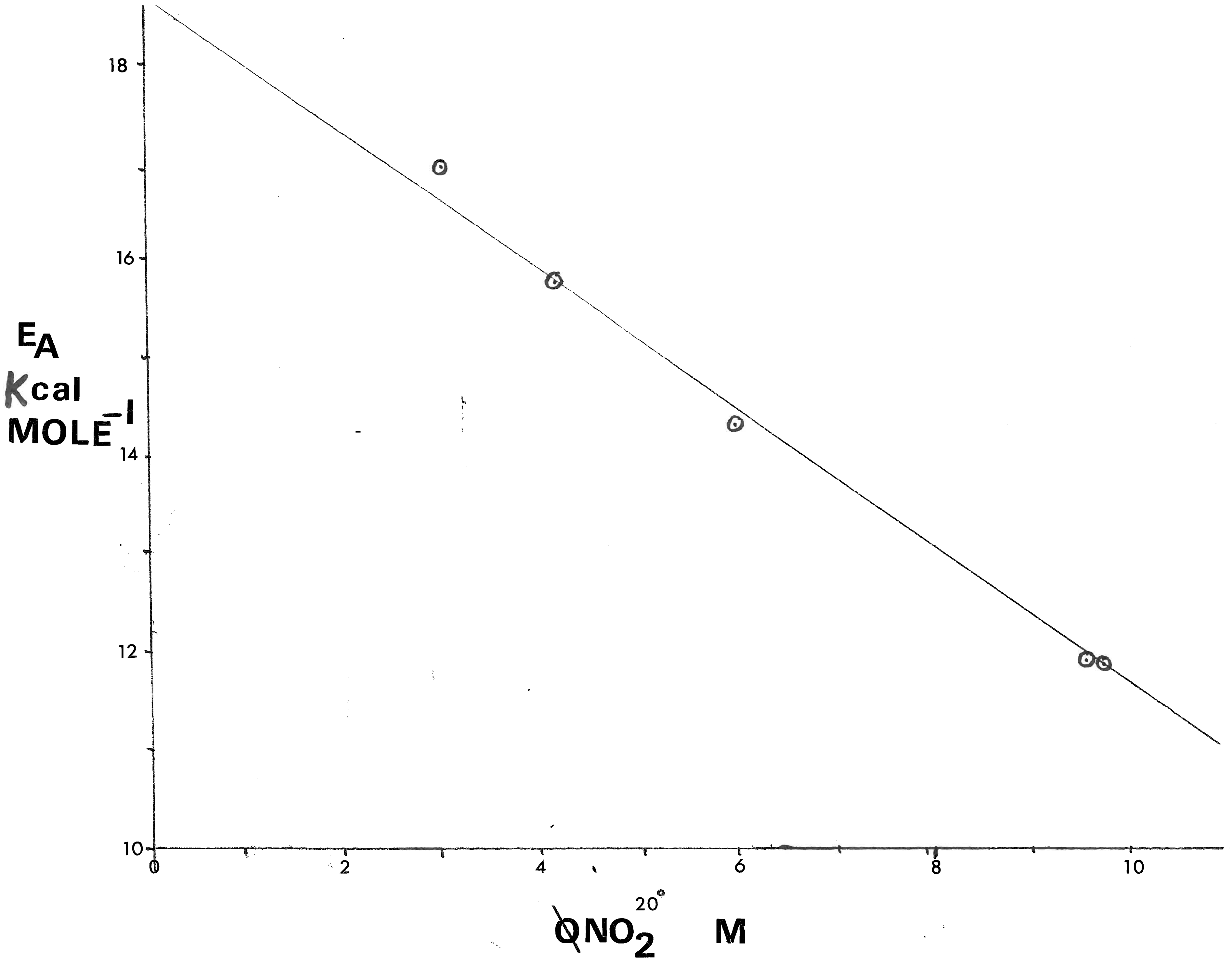
Activation Energy for $CH_3CN.BBr_3-CH_3CN$ as a function of the Nitrobenzene Concentration

E_A Kcal mole^{-1}	(ϕNO_2) M
11.90	9.737
11.90	9.538
14.35	5.964
15.78	4.130
16.94	2.996

From the plot in Figure 12, the activation energy increases with a decreasing nitrobenzene concentration. The extrapolated value for zero nitrobenzene concentration (i.e. the inert solvent approximation for neat dichloromethane) of 18.5 Kcal agrees reasonably well with the dissociation energy of the adduct in solution of 19.1 Kcal.

FIGURE 12

The Effect of Nitrobenzene Concentration on the Activation Energy for CH_3CNBBr_3 - CH_3CN Exchange.


E_A
Kcal
$MOLE^{-1}$
18
16
14
12
10
0
2
4
6
8
10
$\phi NO_2^{20°}$ M

From the same solutions of varying nitrobenzene concentration, the effects of solvent on $\frac{1}{T_{AB}}$ values ($\frac{1}{T_{AB}} = k$,) were also observed and tabulated as in Table 16.

TABLE 16

Effect of Nitrobenzene Concentration on the Rate Constant of Dissociation for $CH_3CN.BBr_3$.

+65°C

$\frac{1}{T_{AB}}$ sec^{-1}	(ϕ-NO_2) Moles $litre^{-1}$
4.65	9.737
4.80	9.538
7.09	6.488
10.37	4.260
15.24	2.750

0°C

$\frac{1}{T_{AB}}$ sec^{-1}	(ϕ-NO_2) Moles $litre^{-1}$
2.83	9.737
2.71	9.538
4.57	6.488
9.49	2.996
10.09	2.750

It was observed for the BBr_3 adduct, as the nitrobenzene concentration is decreased, the rate constant for exchange increases.

The $CH_3CN.BBr_3$ - CH_3CN Exchange was also tried in deuteronitromethane but solvent decomposition proceeded quite rapidly, the solution originally colorless becomes strongly yellow when left at room temperature.

The yellow color produced was attributed to formation of bromine. This was confirmed by the addition of cychohexene, which decolorized the solution. The pH of the solution was about 1 indicating HBr formation. A new NMR peak at 7.40T in the decomposition products corresponds closely with CH_3Br (7.32 T in chloroform).
Our peak was probably shifted upfield because of the more polar CD_3NO_2 . In a recent scrambling study of ether borontrihalide complexes (43), Hamilton, Hartman and Miller (26) also noted that the decomposition of their tribromide complex occurred with formation of methyl bromide. Their trichloride and trifluoride did not decompose.
Our acetonitrile boron tribromide adduct in nitrobenzene left standing at room temperature for several days gradually decomposed. The reason that decomposition in d-nitromethane proceeded quite quickly at room temperature (15 min.) in comparison with nitrobenzene is due to the greater acidity of the nitromethane protons.

Activation Entropy $\Delta S^{\ddagger}$

For the CH_3CNBCl_3 and CH_3CNBBr_3 exchange in nitrobenzene, dichloromethane, $\Delta S^{\ddagger}$ values were calculated from the equation

$$\ln\left(\frac{kh}{KT}\right) = \frac{\Delta S^{\ddagger}}{R} - \frac{E^{\ddagger}}{RT}$$

where k = rate constant (i.e. $\frac{1}{T_{AB}}$)

h = Planck's constant

R = natural gas constant

T = absolute temp

K = Boltzman's constant

Typical $\Delta S^{\ddagger}$ values were calculated as a function of the nitrobenzene concentration and shown in Tables 17 and 18.

TABLE 17

Entropy of Activation for $CH_3CN.BCl_3$ - CH_3CN Exchange in Nitrobenzene, dichloromethane.

$\Delta S^{\ddagger}$ e.u.	E_A Kcal mole^{-1}	$[\phi NO_2]$ M
- 17.1	10.7	6.630
- 8.9	11.9	5.348
+ 6.90	13.62	4.757

TABLE 18

Entropy of Activation for $CH_3CN.BBr_3$-CH_3CN in Nitrobenzene - Dichloromethane.

$\Delta S^{\ddagger}$	E_A	$[\phi NO_2]$
-14.5	11.90	9.737
-14.2	11.90	9.538
- 5.31	14.35	5.964
- 1.75	15.78	4.130
+ 7.87	16.94	2.996

The significance of negative entropies as well as the trend of entropy increase with decreasing nitrobenzene concentration will be treated in the discussion section.

$CH_3CN{\cdot}BF_3$ - CH_3CN Exchange

This adduct was more soluble in nitrobenzene than the others. Since donor-acceptor bond strength is the weakest of the trihalides series it exchanges at the fastest rate and a priori, it must be cooled to a much lower temperature for slow exchange to be observed.

A nitrobenzene - dichloromethane solvent system was tried but it froze at too high a temperature. Neat dichloromethane could not be used because of low solubility at these low temperatures.

A mixed CD_3NO_2 - CH_2Cl_2 solvent system was suitable although slow exchange conditions were not attained.

The exchange reactions were studied in the fast exchange region i.e. above coalescence. We had suspected that CD_3NO_2 would be inert to the BF_3 adduct since the order reactivity was $BBr_3 > BCl_3$ towards solvent decomposition. Neat deuteronitromethane could not be used since its melting point was too high. (m.p. =-35°)

For this system, the coalescence point occurs around - 100° while the region for slow exchange is somewhere about -135° . Although complete separation of the peaks was not accomplished, it was possible to obtain an approximate value for $\delta\nu$, the separation of adduct and free base at the no-exchanging limit.

Activation Energy parameters were calculated on the exchange broadening of the single peak, the temperature range between -60 to -83 was chosen to satisfy the conditions for fast exchange.(28)

i.e. $\frac{I}{T} \gg 2\pi(\delta\nu)$

where $\delta\nu$ = the separation of adduct and free base in the non-exchanging limit

Experimentally $\delta\nu \sim 36.50$ hz $\therefore$ $2\pi(\delta\nu) = 226$ sec^{-1}

i.e. $\frac{1}{T} \gg 226$

where PAB = PB = 0.50

$$\frac{1}{T} = \frac{\pi(\delta\nu)^2}{(W-W_o)}$$

and therefore $\frac{\pi(\delta\nu)^2}{W - W_o} \gg$ 226 for the equation to be applicable

and $(W - W_o) < 18.5$ Hz

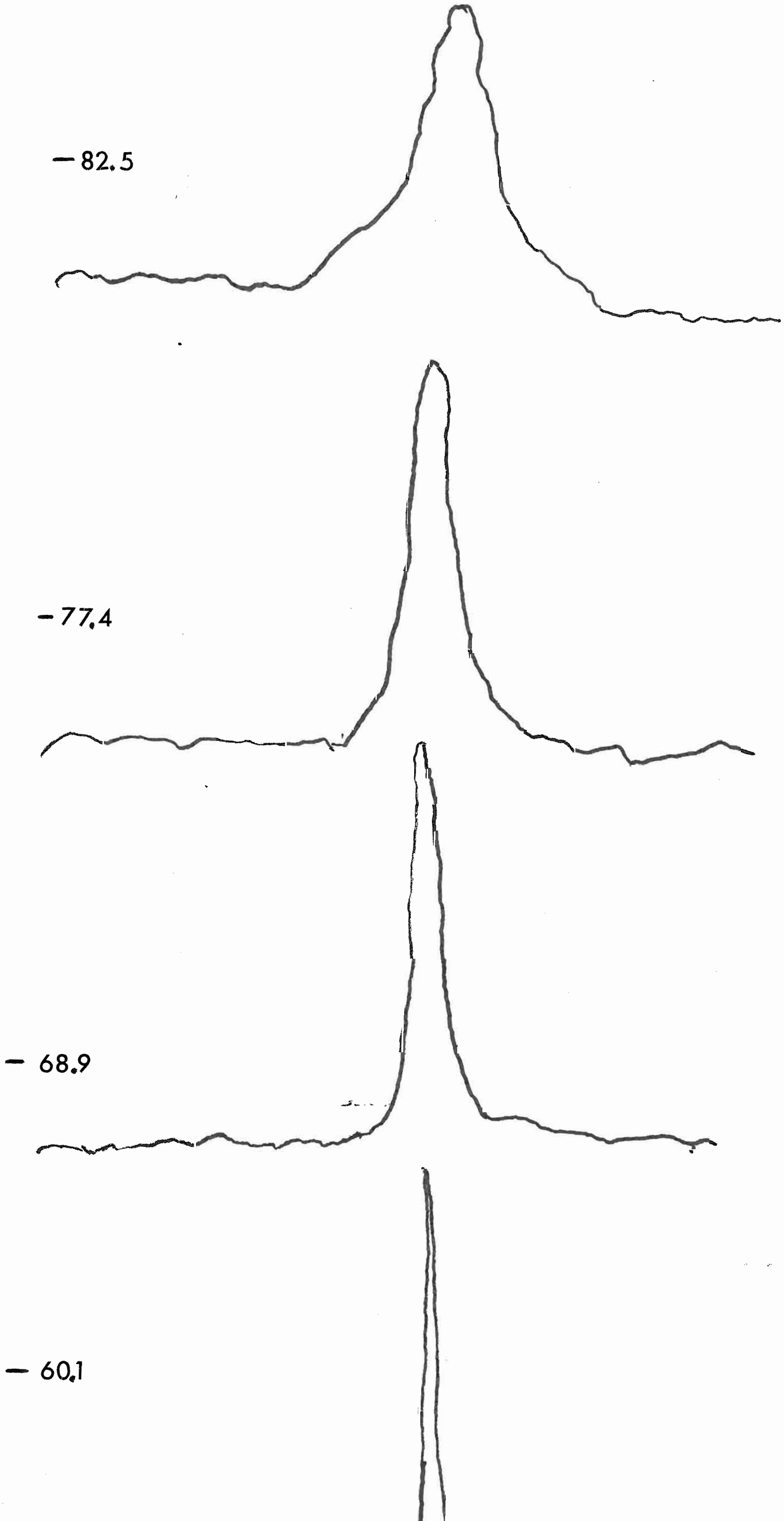
Since for a given solvent system, PAB,PB and $(\delta v)^2$ are constant over the temperature range as indicated by the absence of a shift of the common peak with temperature, a plot of $\ln\left(\frac{1}{(W - W_o)}\right)$ versus $\frac{1}{T}$ was used to calculate the activation energy in most cases.

This procedure simplified the calculations immensely since no detailed knowledge of the effect of solvent mixture on the chemical shifts of the free base and complexed adduct was required.

Figure 13 shows typical spectra obtained from broadening studies on the single peak obtained for fast exchange.

FIGURE13

Exchange in $CH_3CN.BF_3$ - CH_3CN in CD_3NO_2 - CH_2Cl_2 Systems


−82.5
−77.4
− 68.9
− 60.1
200
100

The activation energy could be calculated without prior knowledge of the mechanism of exchange since for either mechanism $\frac{1}{T}$ is related to the rate constant by a product of concentration terms which are to a first approximation independent of temperature. The variation of activation energy with concentrations for $CH_3CN.BF_3$, CH_3CN in the deuteronitromethane, dichlormethane mixed solvent system was studied.

In all samples, the number of moles of adduct was approximately equal to the moles of free base.

From Tables 19 to 22 and corresponding graphs of Figures 14, 15, 16, 17, using the same techniques as for the trichloride and tribromide adducts, one can observe the effects of adding increasing amounts of the inert diluent dichloromethane on the activation energy.

TABLE 19

Solvent Effects on Activation Energies for $CH_3CN{\cdot}BF_3$, CH_3CN Exchange in CD_3NO_2, CH_2Cl_2.

(CD_3NO_2) = 8.09 M

Temp. °C	$(\frac{1}{T}) \times 10^3$ °K^{-1}	(W - Wo) hz	$\frac{1}{T}$ sec^{-1}	$\ln \frac{1}{T}$
-80.2	5.20	4.82	855	6.75
-83.0	5.26	6.12	673	6.51
-86.0	5.34	7.64	539	6.29
-89.2	5.44	10.4	396	5.98
-92.0	5.52	13.21	312	5.74
-95.0	5.61	14.06	293	5.68

E ACT = 6.30 Kcal ± 0.10

FIGURE 14

Activation Energy for $CH_3CN{\cdot}BF_3$- CH_3CN Exchange in Deuteronitromethane Dichloromethane mixed solvent in which (CD_3NO_2) = 8.09M.

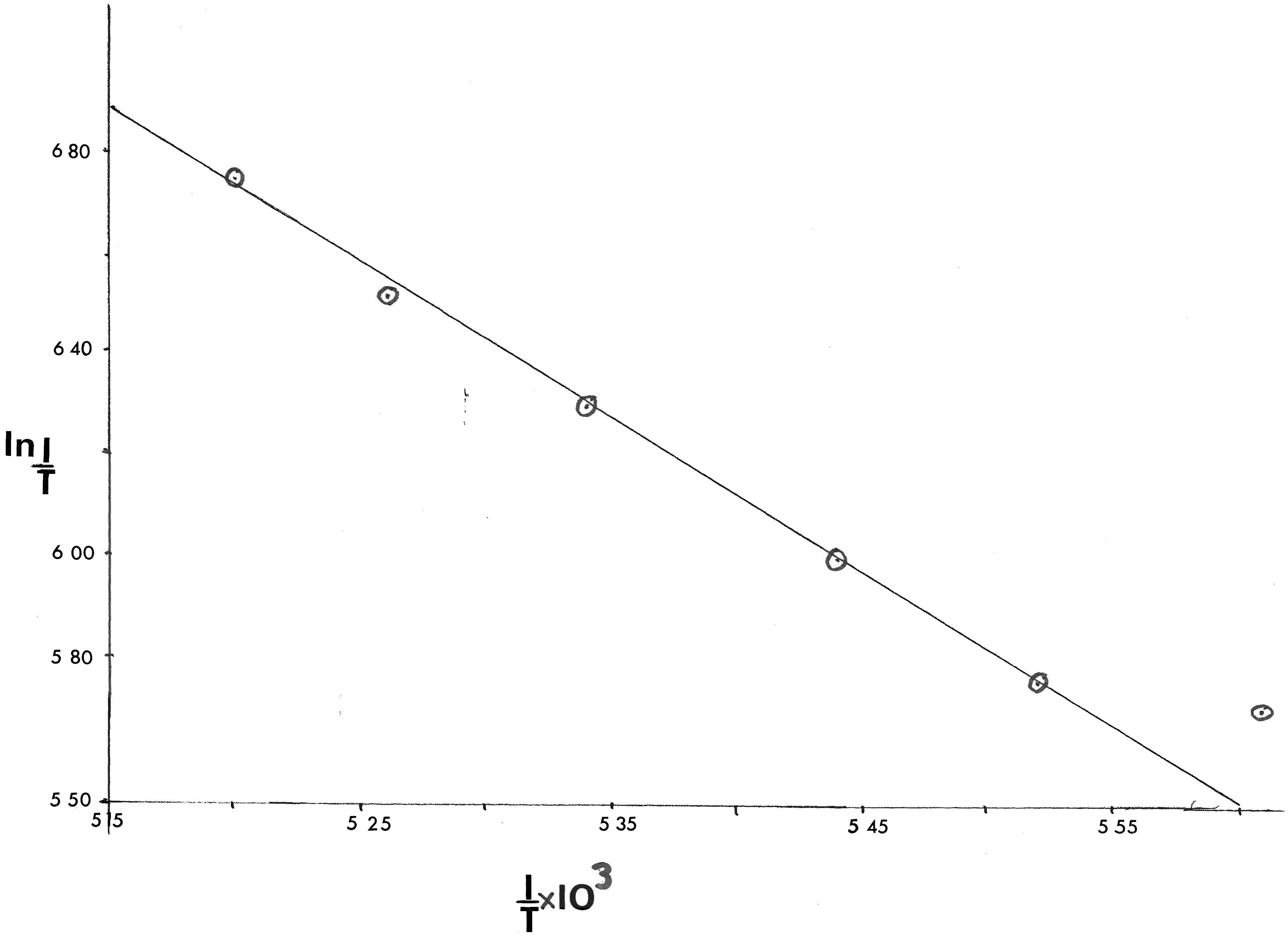

6 80
6 40
6 00
5 80
5 50
ln I/T
5 15
5 25
5 35
5 45
5 55
1/T ×10³

TABLE 20

Effects of Deuteronitromethane Concentration on Activation Energy for $CH_3CN{\cdot}BF_3$ - CH_3CN (CD_3NO_2) = 6.72 M.

Temp °C	(W - Wo) hz	$(W - Wo)^{-1}$ $(hz)^{-1}$	$\ln\left(\frac{1}{W - Wo}\right)$	$\frac{1}{T} \times 10^3$
-65.3	2.71	0.369	-0.997	4.811
-65.5	2.47	0.405	-0.904	4.816
-67.9	3.24	0.309	-1.174	4.872
-72.0	5.66	0.177	-1.732	4.971
-73.1	5.28	0.189	-1.666	4.999
-74.5	5.00	0.200	-1.609	5.034
-76.5	7.80	0.128	-2.056	5.085
-77.5	7.86	0.127	-2.055	5.111
-81.8	15.12	0.0661	-2.717	5.226

E ACT = 7.40 ± 0.50 Kcal.

FIGURE 15

Activation Energy for $CH_3CN{\cdot}BF_3$ - CH_3CN Exchange in CD_3NO_2, CH_2Cl_2

in which (CD_3NO_2) = 6.72 M

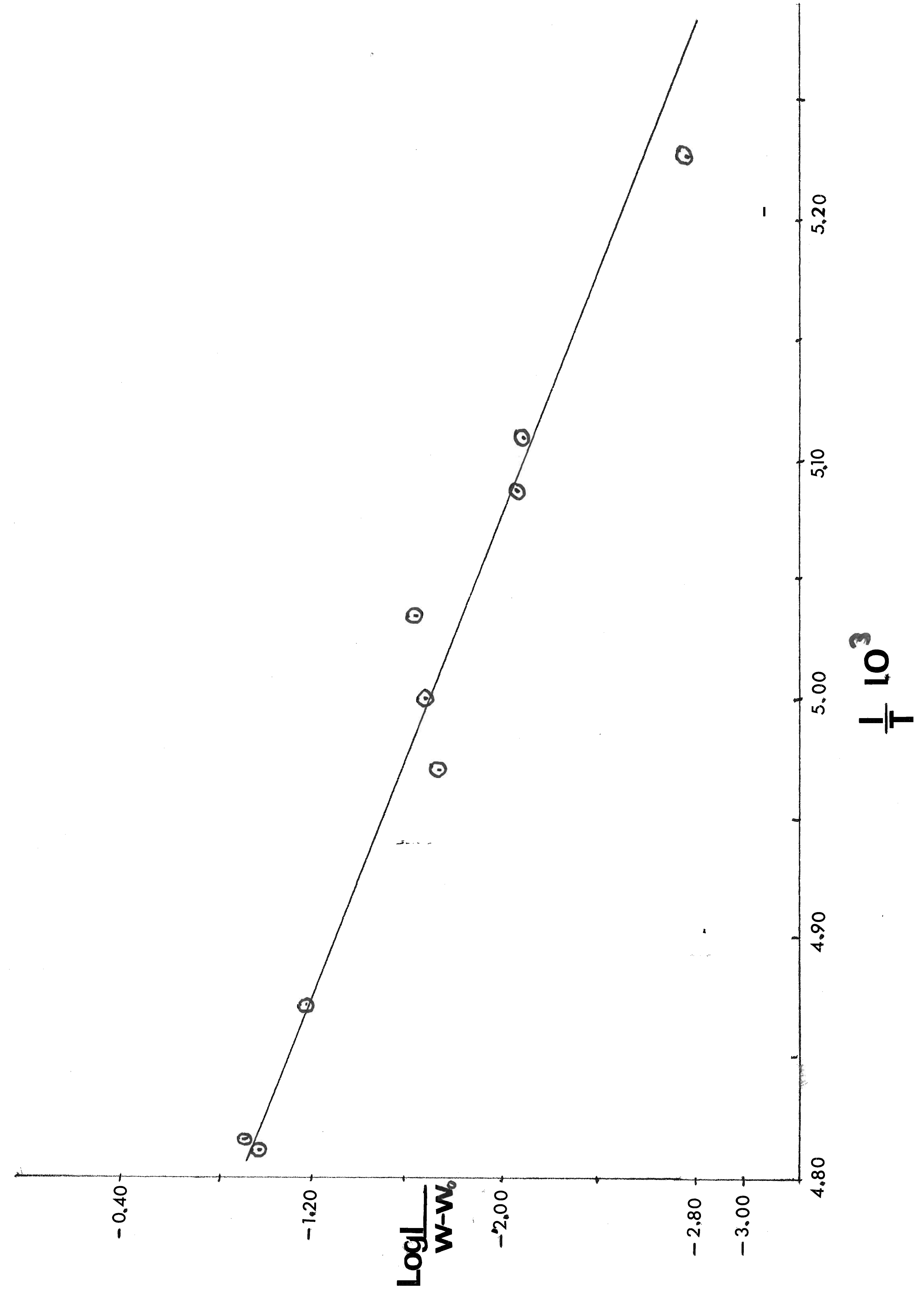

-0.40
-1.20
-2.00
-2.80
-3.00
Log 1/(w-w₀)
4.80
4.90
5.00
5.10
5.20
1/T 10³

TABLE 21

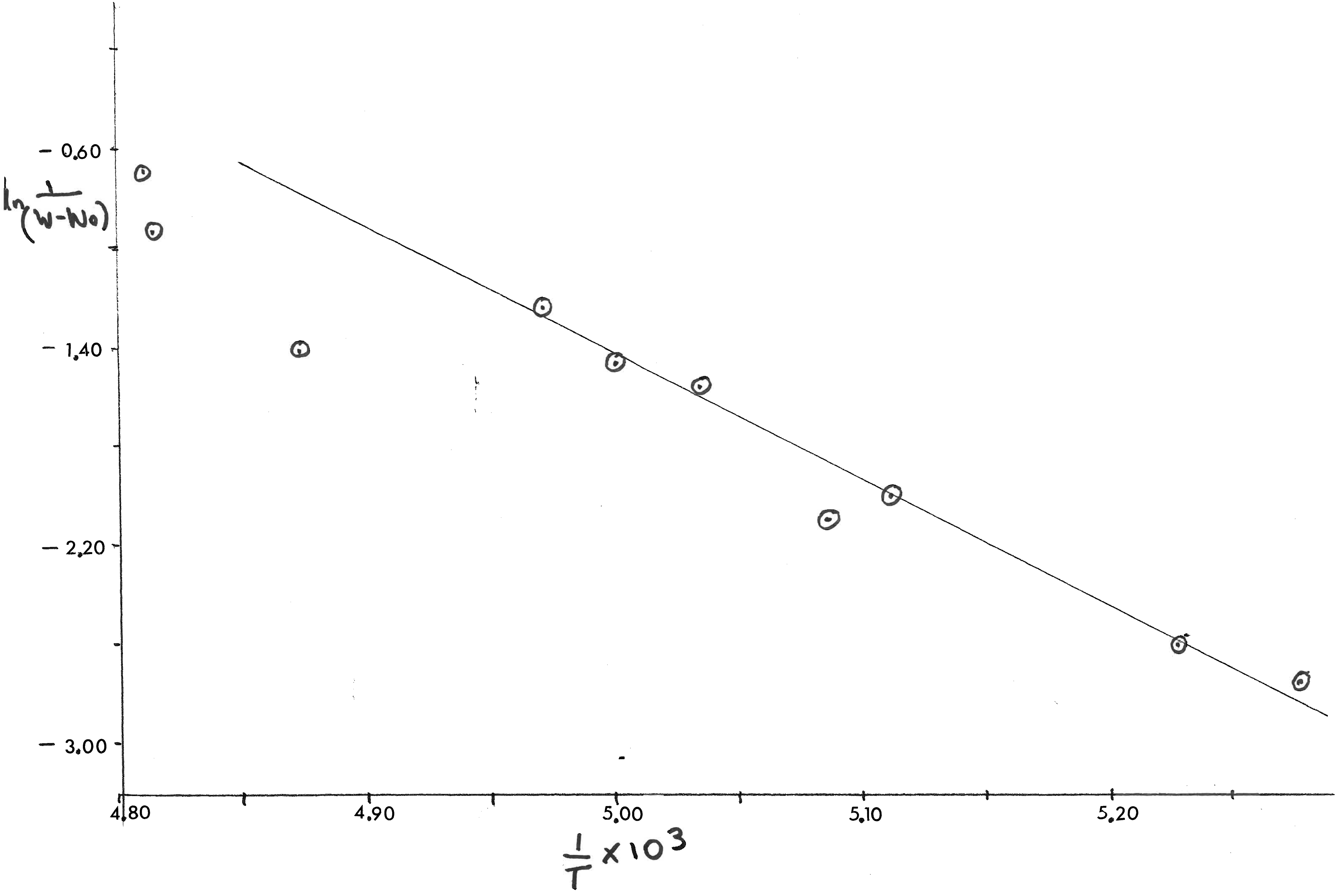
Activation Energy of Exchange of $CH_3CN \cdot BF_3$ - CH_3CN in which (CD_3NO_2) = 5.93 M

Temp °C	(W - Wo) hz	$\left(\frac{1}{W - Wo}\right)$ hz^{-1}	$\ln\left(\frac{1}{W - Wo}\right)$	$\left(\frac{1}{T}\right) \times 10^3$
-65.3	2.01	0.498	-0.697	4.811
-65.5	2.54	0.394	-0.931	4.816
-67.9	4.10	0.244	-1.411	4.872
-72.0	3.49	0.287	-1.248	4.971
-73.1	4.37	0.229	-1.477	4.999
-74.5	4.80	0.208	-1.570	5.034
-76.5	8.20	0.122	-2.104	5.085
-77.5	7.44	0.134	-2.010	5.111
-81.8	13.80	0.0725	-2.624	5.226
-83.7	15.90	0.0629	-2.766	5.278

E ACT ≐ 8.17 ± 0.50 Kcal

Figure 16

Activation Energy for $CH_3CN.BF_3$-CH_3CN in CD_3NO_2,$CHCl_2$ in which (CD_3NO_2) = 5.93 M



- 0.60
- 1.40
- 2.20
- 3.00
$\ln \frac{1}{(W-W_0)}$
4.80
4.90
5.00
5.10
5.20
$\frac{1}{T} \times 10^3$

TABLE 22

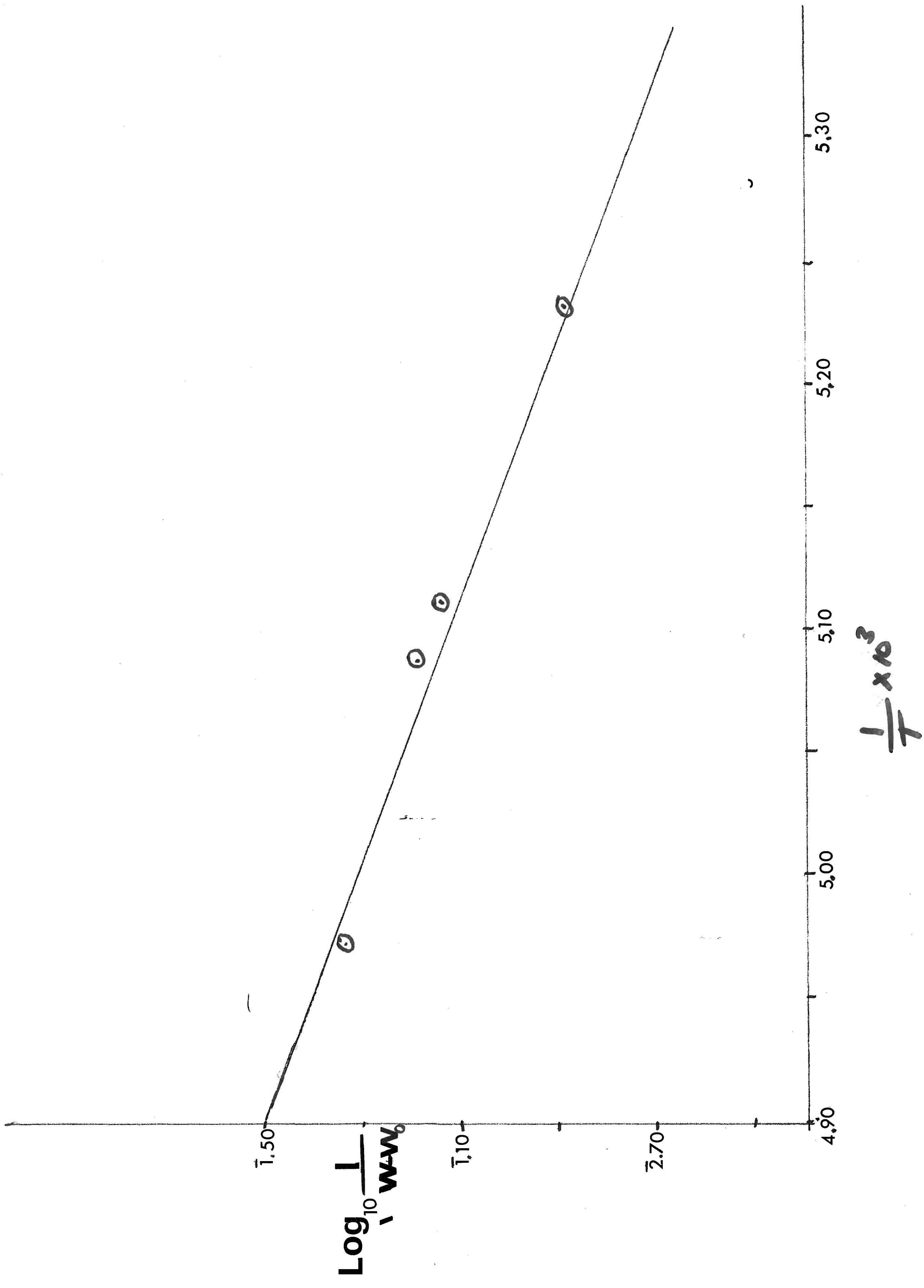
$CH_3CN.BF_3$ - CH_3CN Exchange in CD_3NO_2, CH_2Cl_2 for $(CD_3\ NO_2)$ = 4.45M

Temp	(W - W0) hz	$\left(\frac{1}{W - Wo}\right)$ hz^{-1}	Log 10 $\left(\frac{1}{W - Wo}\right)$	$\frac{1}{T}$ x10^3
-72.0	4.58	0.218	$\bar{1}.338$	4.971
-76.5	6.50	0.154	$\bar{1}.188$	5.085
-77.5	7.25	0.138	$\bar{1}.140$	5.111
-81.8	13.10	0.0763	$\bar{2}.883$	5.226

E ACT = 8.16 ± 0.27 Kcal $Mole^{-1}$

FIGURE 17

Activation Energy for CH_3CNBF_3 - CH_3CN Exchange for (CD_3NO_2) = 4.45 M


$\log_{10} \frac{1}{W-W_0}$
$\bar{1}.50$
$\bar{1}.10$
$\bar{2}.70$
4.90
5.00
5.10
5.20
5.30
$\frac{1}{T} \times 10^3$

From the variation of the activation energy with deuteronitromethane concentration as seen in Table 23, a plot of these parameters extrapolated to the inert solvent condition yielded a value of 11.2 Kcal, the estimated value being about 11 Kcal. Figure18 is a plot of these parameters.

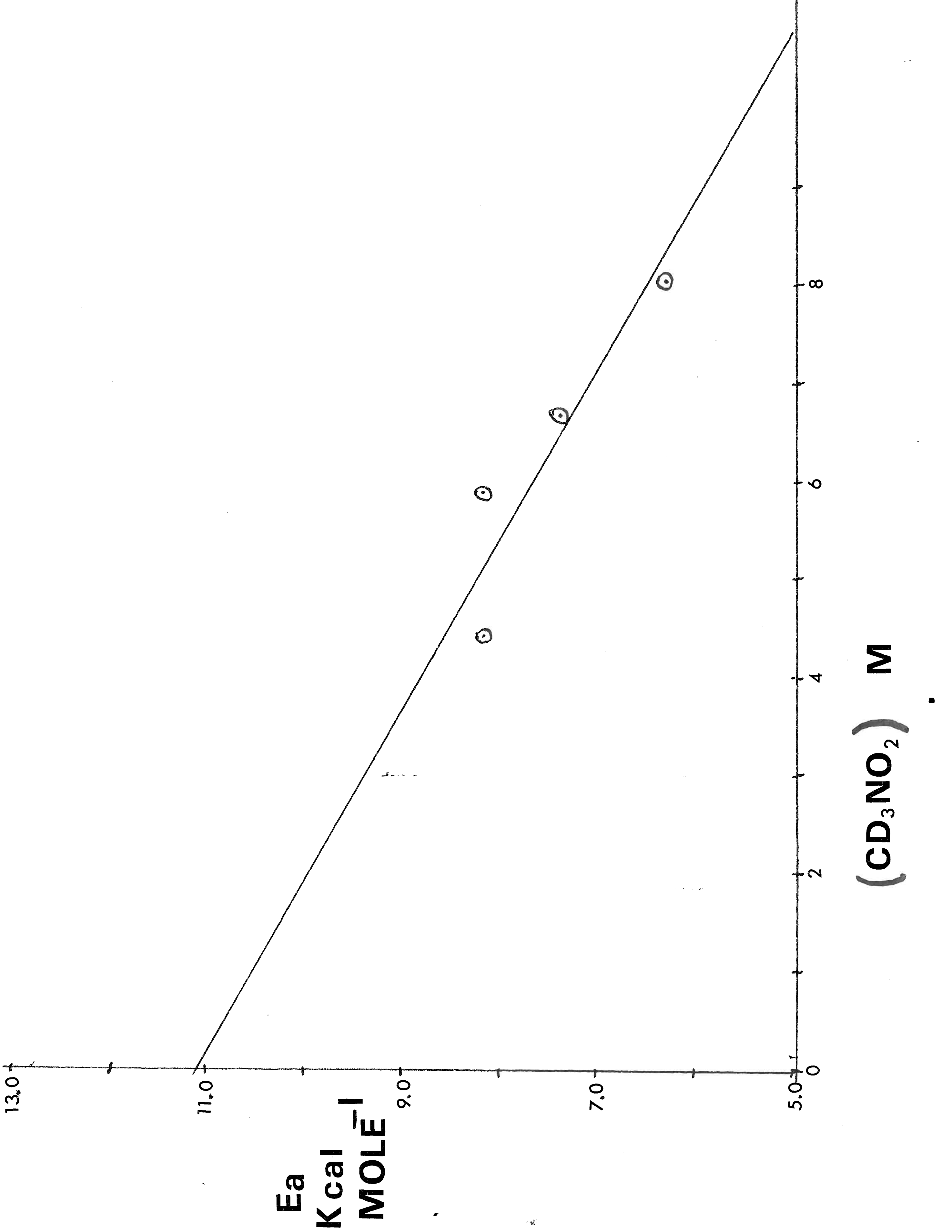
Table23

Activation Energy for CH_3CN Exchange in $CH_3CN.BF_3$-CH_3CN as a function of the Deuteronitromethane Concentration in Dichloromethane

E_a Kcal $Mole^{-1}$	(CD_3NO_2) M
8.16 ± 0.27	4.45
8.17 ± 0.50	5.93
7.40 ± 0.50	6.72
6.30 ± 0.10	8.09

Figure 18

Activation Energy Dependence on the Deuteronitromethane Concentration for $CH_3CN.BF_3$-CH_3CN Exchange


13.0
11.0
9.0
7.0
5.0
Ea
Kcal
MOLE^{-1}
0
2
4
6
8
(CD_3NO_2) M

Samples of $CH_3CN.BF_3$ with excess CH_3CN were made up in which the adduct concentration was kept constant and the acetonitrile concentration varied in the mixed solvent systems. Mole fractions of the species were calculated on the basis of the common peak position relative to the adduct and free base positions in the non-exchanging limit using the equations.

$$P_{AB} = \frac{\nu_{obsd} - \nu_B}{(\delta\nu)}$$

WHERE $\delta\nu$ = separation of adduct and base peak

ν_B = free base position

ν_{obsd} = observed position of common peak

P_{AB} = mole fraction of adduct in solution.

and

$$\frac{1}{T} = \frac{4\pi P_{AB} P_B (\delta\nu)^2}{(W - Wo)}$$

as previously shown.

In this particular solvent system, the d-nitromethane concentration was 7.56M and $\delta\nu$ was approximately 36.5hz.

The equation for calculating $\frac{1}{T}$ was:

$$\frac{1}{T} = \frac{1.674 \times 10^4 \, P_{AB} \, P_B}{(W-Wo)}$$

The data which were obtained are shown in Tables 24 and 25 and a plot of the data shown in Figure 19 .

Table 24

Mechanistic study of $CH_3CN\cdot BF_3$-CH_3CN in CD_3NO_2,CH_2Cl_2 at -71.5^o

P_{AB}	P_B	(W-Wo) hz	$\frac{1}{T}$ sec-1	(AB) x 10 M	(B) x10^2 M
0.786	0.214	4.98	565	1.30	3,54
0.652	0.348	5.64	674	1.30	6.94
0.559	0.441	8.71	474	1.30	10.3
0.444	0.556	7.18	576	1.30	16.3
0.384	0.616	9.09	436	1.30	20.9
0.323	0.677	9.35	392	1.30	27.2
0.260	0.740	6.30	511	1.30	37.0

TABLE 25

Determination of Mechanism for $CH_3CN.BF_3$ - CH_3CN Exchange in CD_3NO_2, CH_2Cl_2 .

-71.5°

$\frac{1}{T}$ /(AB) + (B) litre mole^{-1} sec^{-1}	$\frac{1}{(B)}$ litre mole^{-1}
3378	14.4
2033	9.71
1965	6.13
1285	4.78
974	3.68
1021	2.7

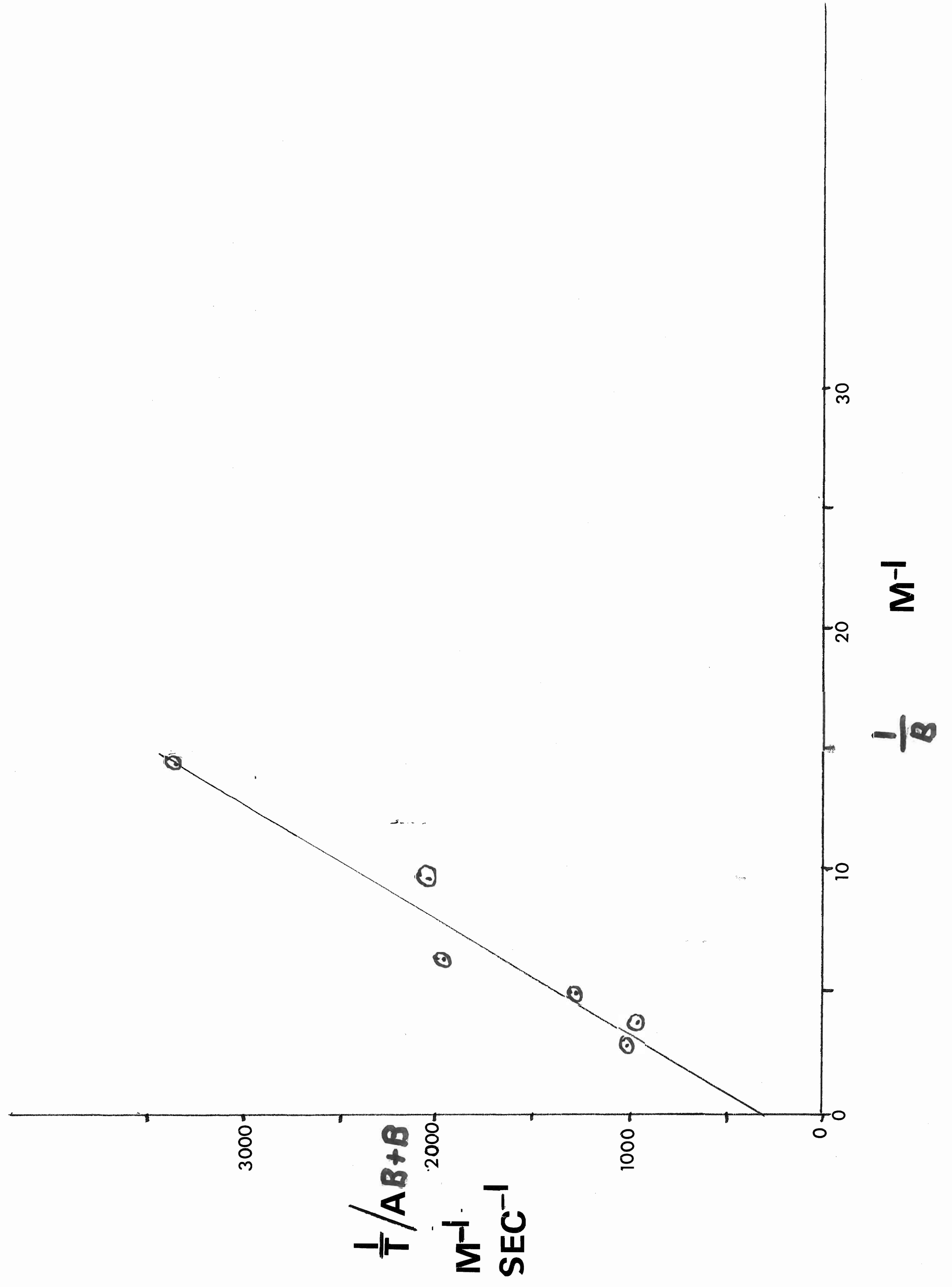
From slope of Figure 19,

$k_1 = 216 \text{ sec}^{-1}$

From intercept $k_2 = 230$ litre moles $^{-1}$ sec^{-1}

Figure 19

Determination of Mechanism for $CH_3CN.BF_3$-CH_3CN Exchange in CD_3NO_2,CH_2Cl_2 at -71.5°


1/T / A B+B
M⁻¹
SEC⁻¹
3000
2000
1000
0
0
10
20
30
1/B
M⁻¹

A similar study was carried out at -65°.

From the data in Tables 26 and 27 and Figure 20 results were obtained in a similar fashion to the previous experiment.

TABLE 26

Effect of Relative Adduct - Free Base Concentration on the Broadening of the Common Peak.

(W - Wo) hz	P_{AB}	P_B	$\frac{1}{T}$ sec^{-1}	(AB) x 10^2 M	(B) x 10^2 M
1.66	0.837	0.163	1376	9.57	1.86
2.07	0.685	0.315	1745	9.57	4.40
2.95	0.563	0.437	1396	9.57	7.42
3.95	0.505	0.495	1060	9.57	9.38
3.06	0.454	0.546	1356	9.57	11.50
1.92	0.408	0.592	2106	9.57	13.9
2.40	0.366	0.634	1619	9.57	16.6
2.00	0.310	0.690	1791	9.57	21.3
1.68	0.216	0.784	1688	9.57	34.7

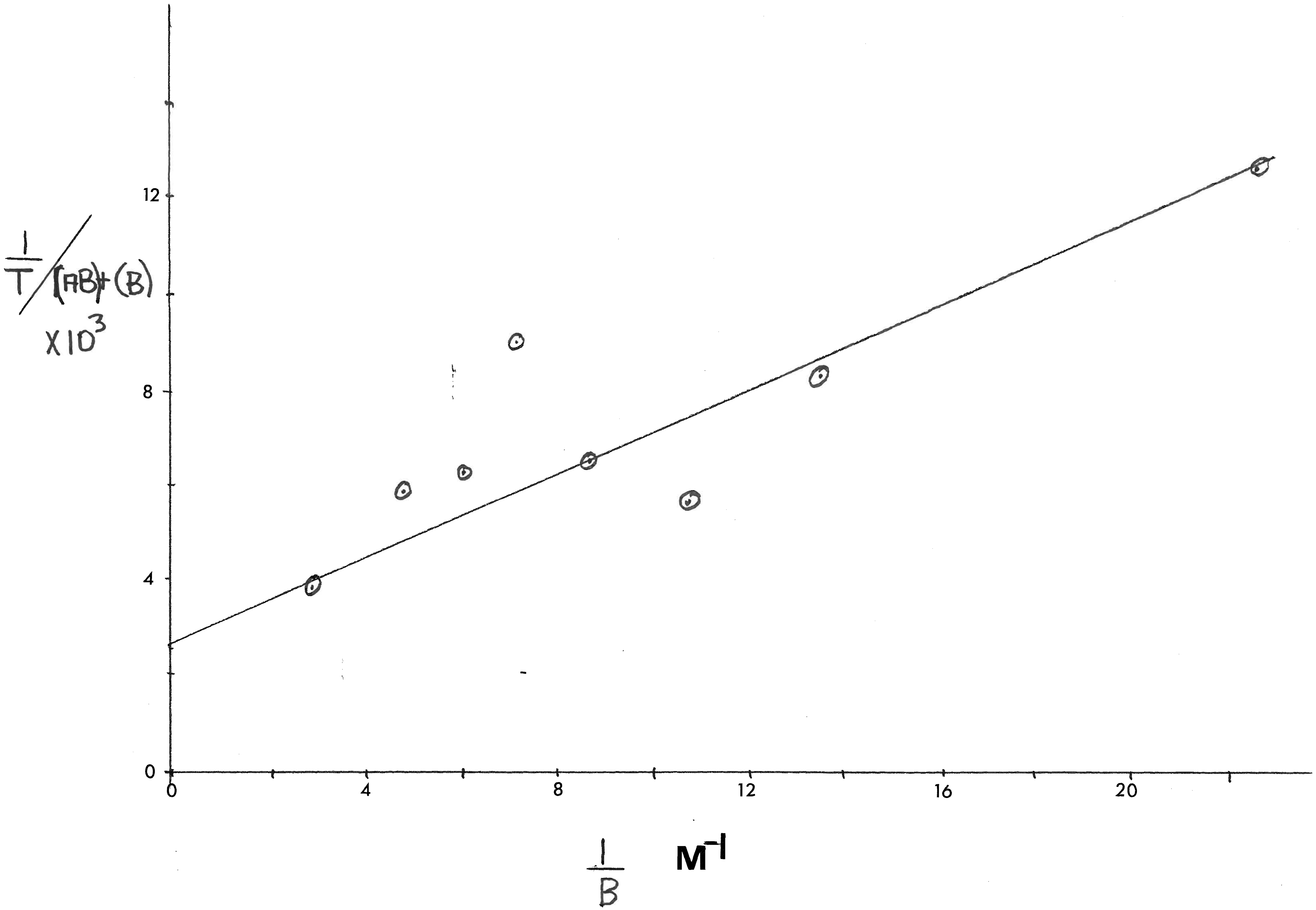
TABLE 27

Parameters for the determination of the Mechanism for $CH_3CN \cdot BF_3$-CH_3CN Exchange in CD_3NO_2, CH_2Cl_2 for (CD_3NO_2) =7.56 M at -65°.

$\frac{1}{T}$ / (AB) + (B) x 10^2 litre $mole^{-1}$ sec^{-1}	$\frac{1}{(B)}$ litre $moles^{-1}$
12.0	53.7
12.5	22.7
8.22	13.5
5.60	10.7
6.44	8.70
8.98	7.20
6.19	6.04
5.80	4.70
3.81	2.88

FIGURE 20

Mechanistic Study of the $CH_3CN{\cdot}BF_3$ - CH_3CN Exchange in CD_3NO_2, CH_2Cl_2 at -65° for (CD_3NO_2) = 7.56 M


$\frac{1}{T} / [AB] + (B)$
X 10^3
12
8
4
0
0
4
8
12
16
20
$\frac{1}{B}$ M^{-1}

at -65°

$$k_1 = 423 \text{ sec}^{-1}$$

$$k_2 = 2800 \text{ litre mole}^{-1} \text{ sec}^{-1}$$

Due to the systematic errors involved in the calculations as seen from the scatter of values on the graph, the error involved in the interceptis quite large and it is not really possible to decide unambiguously in favor of either one or both simultaneous mechanisms.

The prescence of a non-zero slope (the slope would be zero if dissociation did not occur) might indicate a dissociative scheme at least.

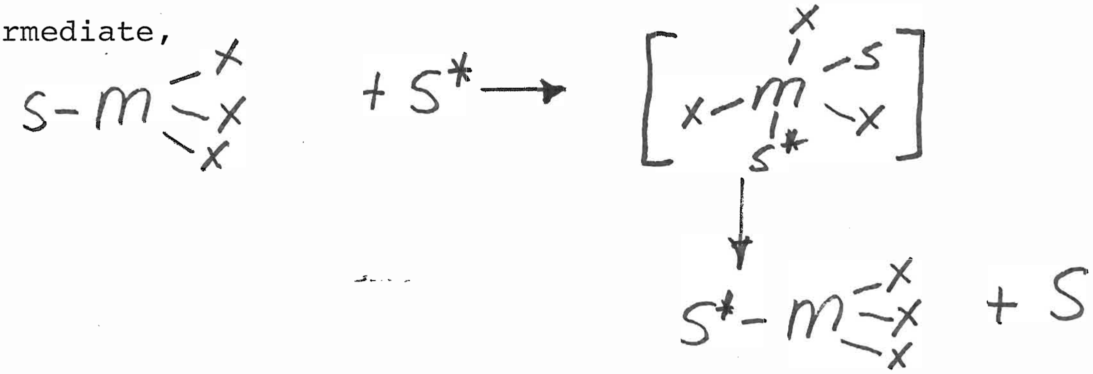
A rough calculation of the activation energy from the values of k_1 at -65° and -71.5° gives the result as 8.35 Kcal which is quite reasonable for this CD_3NO_2 concentration.

DISCUSSION

One question that arises is an outcome of the trimethylgallium amine exchange cited in the introduction. The dissociation energy of these adducts are about 19 Kcal, similar in energy to our acetonitrile trichloride and tribromide complexes. However, the mechanism of exchange in their systems were strongly influenced by steric effects - a substitution of a smaller hydrogen for a large bulky methyl groups on the amine increasing the favourability for collision mechanism.

However, the other factor to be considered is the stability of the transition state.

For group III adducts, the transition state for preliminary collision between a free base or acid molecule with an adduct which is originally in a four co-ordinate state is a five co-ordinate intermediate,



which can then give a stable four co-ordinate product in which exchange of base has occured.

Gallium has d orbitals of suitable energy available with which to expand its co-ordination number. In fact five co-ordinate compounds of Aluminum, Gallium and Indium have been reported in the literature.

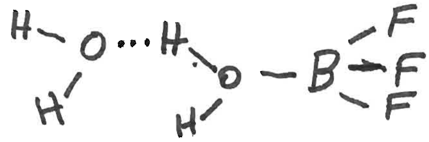
i.e. - the $MX_3,2NMe_3$ series (44), (45), (46),(47),(48),(49),(50).

The ease of expansion of the coordination number of these elements is one of the criteria in determining the feasibility of the collision induced intermediate.

Boron differs from the remaining group III metals in that its maximum co-ordination number is four. Since there is no d orbitals of suitable energy available in the n=2 period for additional bonding, it cannot readily form a five member transition state.

No five co-ordinate boron compounds have ever been isolated. Although a hydrate of boron trifluoride $BF_3.2H_2O$ was shown to exist at low temperature by NMR, its structure was determined to be a four co-ordinate boron with one water molecule loosely bonded to the other bond via hydrogen.

i.e.



Cowley and Mills (39) have shown that for the exchange reaction of $(CH_3)_3NB(CH_3)_3$ with excess acid or base, the rate determining step is the dissociation of the adduct. Oliver et al (51) have argued that for the above adduct, steric hindrance was the only reason why the collision mechanism was not favoured. In our particular systems

acetonitrile is one of the least sterically hindered bases since it is linear and has hydrogen atoms as the only substituents. Molecular models show that for collision of tetrahedral boron, the hydrogen of the acetonitrile are so far removed from the bromines or chlorines that no steric hindrance between them could occur at all. According to Oliver's argument, then, our system would be most favored to exchange via collision.

Since our systems, in fact, exchange via dissociation, we must conclude that for exchange in boron systems, the factor that determines the dissociation mechanism is the inability of the boron atom to readily achieve a five co-ordinate transition state.

Of course, this type of argument may not be entirely correct since the molecular ion $CH_5^{\oplus}$ has been observed spectroscopically.

For B - N adducts, the amount of electronic charge transferred will be related to the strength of the adduct bond and also to the magnitude of the dipole moment (22). In the acetonitrile boron trihalide adducts, the dissociation energy varies as $BBr_3 > BCl_3 > BF_3$ indicative of the relative strengths of the bonds (14). This trend is also borne out for the trimethylamine-boron trihalide adducts in which the dipole moments of the BBr_3 , BCl_3 and BF_3 adducts are 5.57, 5.13 and 4.04D respectively (3).

Our study of the kinetics of acetonitrile boron trihalide exchange with excess acetonitrile indicated that slow exchange conditions are achieved at higher temperatures for the BBr_3 adduct (-15° to +15° in nitrobenzene) than for the BCl_3 adduct (-30° to -55° in nitrobenzene dichloromethane) or the BF_3 adduct ($<$ -130° in deuteronitromethane dichloromethane). This means that at a given temperature the BF_3 adduct is exchanging at the fastest rate, the BCl_3 at the intermediate rate and the BBr_3 adduct at the slowest rate. Since the dissociation mechanism has definitely been shown to operate as the rate controlling step for BBr_3 and BCl_3 exchange while for BF_3 only tentatively so, the relative exchange rates of the adducts are entirely compatible with their relative bond strengths although solvent effects have also been shown to affect this exchange rate.

SOLVENT EFFECTS

It would have been most suitable to use neat dichloromethane as the solvent for these exchange studies since it has a low melting point (-95°), is relatively inert and does not have any significant coordinating properties.

Unfortunately, although the adducts were soluble to some extent at room temperature, they tended to precipitate out at lower temperatures in this solvent. The insolubility in this non-polar media can probably be attributed to the relatively high dipole moments of the adducts since they are more soluble in the polar, high dielectric constant solvents, nitromethane and nitrobenzene.

Nitrobenzene, as a co-ordinating solvent, might be expected to lower the activation energy via the formation of a nitrobenzene boron trihalide intermediate i.e.- $CH_3CN\ldots BCl_3\ldots \text{Ø}NO_2$

When neat nitrobenzene was used as the solvent for the BBr_3 adduct, the activation energy for this process was 11.9 Kcal. This was considerably lower than 19.1 Kcal, the dissociation energy of the adduct in solution. Also for the first BCl_3 system studied in which the solvent ratio of the dichloromethane to nitrobenzene was 1.19 to 1 by volume, an activation energy of 12.8 Kcal was obtained which is compared with 18.1 Kcal for dissociation in solution.

On explanation might have been that the process we observed was actually a pseudo first order reaction which involved a collision with a solvent molecule:-

$$AB + S \overset{k}{\rightleftharpoons} AS + B \qquad \text{slow}$$

$$AS + B^* \longrightarrow AB^* + S \qquad \text{fast}$$

in this case $\dfrac{1}{T_{AB}} = k.\,(S)$ and $\dfrac{1}{T_B} = k.\,(S)\,\dfrac{(AB)}{(B)}$

For a given system studied, the nitrobenzene concentration was kept constant and thus our value of $\dfrac{1}{T_{AB}}$ obtained would appear constant but might vary with solvent concentration. As seen in the experimental section, as the nitrobenzene concentration of the solvent was increased the $\dfrac{1}{T_{AB}}$ value in fact, decreased. This is in exact opposition to to that predicted by solvent collision in which $\dfrac{1}{T_{AB}}$ should increase when the nitrobenzene concentration increases. We therefore conclude that the solvent does not participate via simple collision.

We are postulating that the exchange proceeds through a solvent cage intermediate (36), which will lower the activation energy for exchange.

i.e.- $(AB) \longrightarrow (A...B) \longrightarrow A + B$ slow

$A + B^{*} \longrightarrow AB^{*}$ fast

We found that the activation energy for exchange increased with decreasing concentration of nitrobenzene and that the exchange rate constant also increased with a decreasing concentration of nitrobenzene. These observations can be explained as follows:-
In a higher nitrobenzene concentration, the solvent cage will be very strong and hence the activation energy will be depressed to a greater extent. For a low nitrobenzene concentration, the solvent cage should be much weaker and the activation energy should increase.

The solvent cage will slow down the apparent rate of reaction since the separated acid and base inside the solvent cage will recombine at a much faster rate than that at which they diffuse out of the cage. Since exchange with a free base molecule can only occur once the acid molecule has migrated out of the cage, the diffusion rate is therefore the rate determining step for exchange.

In a strong solvent cage (i.e. high nitrobenzene concentration), escape of an acid molecule would be most inhibited and recombination inside the cage takes place at a much faster rate. As the nitrobenzene concentration of the system is decreased, the solvent cage becomes weaker allowing migration outwardly to proceed at an increasing rate.

In other words, as the nitrobenzene concentration decreases, the rate of exchange will increase. This is in accord with our observations.

The viscosity of nitrobenzene at room temperature is greater than that of dichloromethane. At low temperatures, one might expect a mixed solvent with a high concentration of nitrobenzene to have a greater viscosity than that which has a low concentration. However, the differences in viscosity of the solutions cannot be appreciable since the TMS width at half height is essentially constant for all solutions. Therefore, in the temperatures and concentration ranges over which our results were obtained, viscosity broadening does not appear in itself to be a significant factor. In any case, this could be taken into account in the natural line width correction.

In a recent paper on group III exchange reactions, Oliver (52) et al have stated that coordinating solvents decrease the rate of exchange relative to an inert solvent,although they have not as yet published any data to corroborate their observations.

Another point in favour of the solvent cage intermediate was the entropy of activation for exchange. For both BCl_3 and BBr_3 systems negative values for the entropy of activation were obtained. Normally one expects a positive $\Delta S^{\ddagger}$ for a dissociative process since this transition state intermediate is "less ordered". However, our negative values indicated that the transition state is more highly ordered than the original state and this is consistent with the properties of the solvent cage. As the nitrobenzene concentration decreases, the solvent cage becomes progressively weaker i.e.-less ordered and the $\Delta S^{\ddagger}$ values reflect this trend in becoming more positive.

One can also approach the solvent effects on activation energy from an electrostatic point of view. One can regard the B - N bond as a dipole $\overset{\delta-}{B} - \overset{\delta+}{N}$, in which the boron and nitrogen atoms are held together by coulombic attraction of magnitude:-

$$F = \frac{\delta^2 e^2}{\epsilon (r_{B-N})^n}$$

where F= coulonbic force of attraction

δ= amount or fraction of electronic charge transfered

e= charge of an electron

ϵ= dielectric constant of medium

r_{B-N}= length of BN bond

n= exponent

And the energy required to separate the charges is given by the expression $E = \dfrac{-\delta^2 e^2}{\epsilon (r_{B-N})^{n-1}}$

Since the boron nitrogen bond distance and the value of δ are constants for a given system, the energy E required to separate the charges will vary inversely as the dielectric constant of the medium. Nitrobenzene with dielectric constant = 34 is much greater than that of methylene chloride = 9

In the mixed solvent systems, a higher concentration of nitrobenzene will increase the dielectric constant of the medium. A higher dielectric constant will lead to a smaller energy required for charge separation i.e.- As the concentration of nitrobenzene is increased, the activation energy of dissociation should decrease. This agrees with our observation that as the ϕNO_2 concentration increases, the activation energy decreases.

Recently Schmulbach and Ahmed(53) , in a conductometric study of boron halides in acetonitrile have shown that the BBr_3 and BCl_3 exhibit weak electrolytic behaviour and have shown that considerable amounts of $BCl_4^{\ominus}$ and $BBr_4^{\ominus}$ are present in solution. This brings up the possibility of ionic species being involved in the exchange reactions.

The following steps can be postulated for some exchange involving ion pairs.

$$1)\quad 2\ CH_3CN.BCl_3 \overset{k_1}{\rightleftharpoons} \left((CH_3\ CN)_2\ BCl_2^{\oplus}\ ,\ BCl_4^{\ominus} \right) \xrightarrow{k_2} (CH_3CN)_2BCl_2^{\oplus} + BCl_4^{\ominus}$$

$$2)\quad CH_3CN^* + (CH_3CN)_2BCl_2^{\oplus} \longrightarrow (CH_3CN)_2^{*}\ BCl_2^{\oplus} +$$

The rate determining step being the separation of the ion pairs.

$$\text{Rate} = \frac{(AB)}{T_{AB}} = \frac{d\ (AB)}{dt} = k_2\ (\text{ion pair}) = k_2K_1\ (AB)^2$$

$$\frac{1}{T_{AB}} = k_2\ K_1\ (AB)$$

However, we found $\frac{1}{T_{AB}}$ values independent of concentration terms

and so this scheme is also not valid. Another possible mechanism may involve the dissociation of the $(CH_3CN)_2\ BCl_2^{\oplus}$ as

$$(CH_3CN)_2\ BCl_2^{\oplus} \xrightarrow{k_3} CH_3CN + CH_3CN.BCl_2 \quad \text{slow}$$

$$CH_3CNBCl_2 + CH_3CN^* \longrightarrow (CH_3CN)^{*}(CH_3CN)BCl_2 \quad \text{fast}$$

$$-\frac{d(AB)}{dt} = \frac{(AB)}{T_{AB}} = k_3\ (CH_3CN)_2\ BCl_2^{\oplus}\ )$$

$$= k_3k_2K_1\ (AB)^2$$

$$\frac{1}{T_{AB}} = k_3k_2K_1\ (AB)$$

and again concentration terms are involved which rule out this possible pathway.

Other possible pathways involving concentration can also be eliminated.

For an ionic mechanism, one would expect that the higher dielectric constant of the solution would promote an increased rate of exchange. In our experiments, we observed the exact opposite i.e.- the rate of exchange, $\frac{1}{T_{AB}}$ decreased as the dielectric constant(Nitrobenzene concentration) increased.

This conclusively rules out ionic mechanism as an important exchange reaction . Neat Deuteronitromethane was also used as a solvent for the $CH_3CN.BCl_3$, CH_3 CN system.

Slow exchange conditions were attained about 20° higher (-35 to -16) for this solvent than for the mixed nitrobenzene, dichloromethane solvent (-55 to -35). This again demonstrates the effect of solvent on the rate of exchange. In both solvents, $\frac{1}{T_{AB}}$, was independent of concentration terms, indicating dissociation as the primary pathway. In the deuteronitromethane solvent, the activation energy was 13.3 Kcal while for neat nitrobenzene, the extrapolated value was 7.3 Kcal.

This observation agrees with the idea that nitrobenzene is a stronger Lewis base than nitromethane and would be expected to have a greater effect on depressing the activation energy than nitromethane.

For the $CH_3CN.BF_3$, CH_3CN system in CD_3NO_2, CH_2Cl_2 a dependence of the activation energy on the concentration of nitromethane was also observed. Similar to the tribromide and trichloride systems, the activation energy decreased as the d- nitromethane concentration increased and can be attributed to solvation effects as well. Unfortunately, since only the fast exchange region was studied, it is not possible to predict the dependence of the $\frac{1}{T_{AB}}$ value on the d-nitromethane concentration although the trend is expected to be similar to the other adducts.

Ambiguities exist in the mechanistic studies on the single peak. It may be that both collision and dissociation may be operating simultaneously since steric hindrance of the fluorines is much less than the chlorines or bromines but due to the systematic errors inherent in the equation used, this cannot be said with certainty.

SUMMARY OF RESULTS OBTAINED

1. The exchange of $CH_3CN.BBr_3$ and $CH_3CN.BCl_3$ with excess base proceeds via a dissociative mechanism while for the CH_3CNBF_3 adduct, the mechanism is uncertain.

2. Solvent participation of nitrobenzene and CD_3NO_2 in lowering the activation energies for dissociation of the CH_3CNBBr_3 and CH_3CNBCl_3 adducts as well as for the CH_3CNBF_3 adduct occurs via a proposed solvent cage intermediate.

3. As the concentration of basic solvent is increased, the rate of exchange decreases and this has been rationalized on the basis of the solvent cage.

4. The activation energies extrapolated to inert solvent conditions for the $CH_3CN.BBr_3$, $CH_3CN.BCl_3$ and $CH_3CN.BF_3$ adducts agree very well with the calculated dissociation energies of Lockhart and Blackborow .

	EXPERIMENTAL	LOCKHART et al	
$CH_3CN.BBr_3$	18.5	19.1	(23)
$CH_3CN.BCl_3$	17.65	18.1	(23)
$CH_3CN.BF_3$	11.2	11	

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