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RELAXATION KINETICS IN GASEOUS LEWIS ACID/BASE SYSTEMS*: THE PROTOTYPE, $(CH_3)_2O+BF_3 \leftrightharpoons (CH_3)_2O:BF_3$*,**

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ABSTRACT

When a gaseous mixture of ether, boron trifluoride and their complex, at equilibrium (temperature range 290-335 K), is slightly perturbed by the imposition of a rapid temperature jump ≈ 3 to 6°, the system relaxes to a new equilibrium. From the dependence of the measured relaxation time on the pressure of the reagents, the initial temperature and the pressure of a diluent gas (argon), we derived rate constants for the dissociation and association processes, based on published values of the equilibrium constant, $K_{eq}(T)$. The temperature dependence of the dissociation rate constant leads to an activation energy (2nd order regime), for comparison with the O-B (donor-acceptor) bond dissociation energy.

INTRODUCTION

In 1923 Lewis [1] proposed that the stability of complexes of the type $R_3N:BX_3$ is due to the sharing of an electron pair from the donor atom, by transfer to an acceptor atom with a two-electron vacancy in its octet. During the following 65 years the reports on many aspects of Lewis acid/base complexes grew to a vast literature. Mulliken first formulated their electronic structures as charge-transfer processes, $\psi(A:B) = a\psi_0\ (A\text{-}B) + b\psi_1\ (A^-B^+)$; since then numerous theoretical analyses of charge-transfer spectra have been published based on this formalism. These were extensively reviewed by Mulliken and Person [2]. There are reports on the geometry of the complexes (electron diffraction and microwave spectroscopy), spectra (NMR, IR, Raman and UV), and thermochemistry. However, to our knowledge no studies on reversible rates of such association/dissociation processes were under-

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*Dedicated to Professor E. Bright Wilson Jr.

**This is paper X of our series on "Intramolecular Conversions Over Low Barriers".

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taken. The several kinetic investigations that we encountered in our extensive literature survey were limited to rates of unidirectional (irreversible) associations, each measured at a single pressure and temperature; no activation energies could be derived.

In an ingenious adaptation of the Polanyi flame-diffusion technique, Kistiakowsky and Klots [3] measured the rates of association of BF_3 with a series of amines, under diffusion limited conditions. These studies and derivative measurements were reviewed by Bauer [4]. At ambient temperatures, the bimolecular rates indicate association collision efficiencies that range from 0.001 (for NH_3) to 0.06 (for Me_3P). Association rates of BH_3 with various bases were reported by Fehlner [5] and by Pasternack et al. [6]. With trimethylamine the collision efficiency for sticking is an order of magnitude greater for BH_3 than BF_3.

Study of a system with all its components in the gas phase permits measurement of an activation energy for dissociation (E_a), which theoretically could be either greater or approximately equal to the thermochemical dissociation energy ($\Delta E°$: ref. 2, p. 225). However, it is also conceivable that E_d could be less than $\Delta E°$, when dissociation is augmented by a displacement step

$$\begin{tikzcd}
B_1{:}A + B_2 \arrow[r, shift left] & {[B_1AB_2]} \arrow[l, shift left] \arrow[r, shift left] & B_1 + A{:}B_2 \arrow[l, shift left] \arrow[d, shift left] \\
 & & B_2 + A \arrow[u, shift left] \arrow[ull, dashed]
\end{tikzcd} \qquad (1)$$

This plausible alternative to direct bond fission was found to apply to the dissociation of dimeric formic acid [7]. It was confirmed by the observations that whereas the system kinetics were invarient to added Ar (up to 600 torr), the rate increased linearly with pressure of various added hydrogen-bonding species.

Besides providing a probe for the mechanism of donor–acceptor association/dissociations, a detailed kinetic analysis would show whether in sufficiently energized molecules intramolecular vibrational relaxation controls the dissociation rate of the weak dative bond (≈ 13.6 kcal mol^{-1} [8])*, and hence whether RRKM theory for a highly flexible transition structure is applicable [9]. It may be that some of the molecular oscillators in the complex are not fully coupled to the O–B stretching vibration (which becomes the reaction coordinate). If this were the case, the experimental activation energy at the high pressure limit would be higher than the bond dissociation energy. It is worth noting that for this particular A/B pair association induces a minimal change in the structure of the ether and hence in its IR spectrum (Fig. 1) but converts the boron trifluoride from planar D_{3h} to tetrahedral coordination, with corresponding lengthening of the B–F distances (1.313 to 1.358 Å [10];

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*For compilation of ΔH^0 values for BF_3 (g) + B (soln) → B:BF_3(soln) in non-protogenic solvents see ref. 8a; for $Me_2O + BF_3$ see refs. 8b,c.

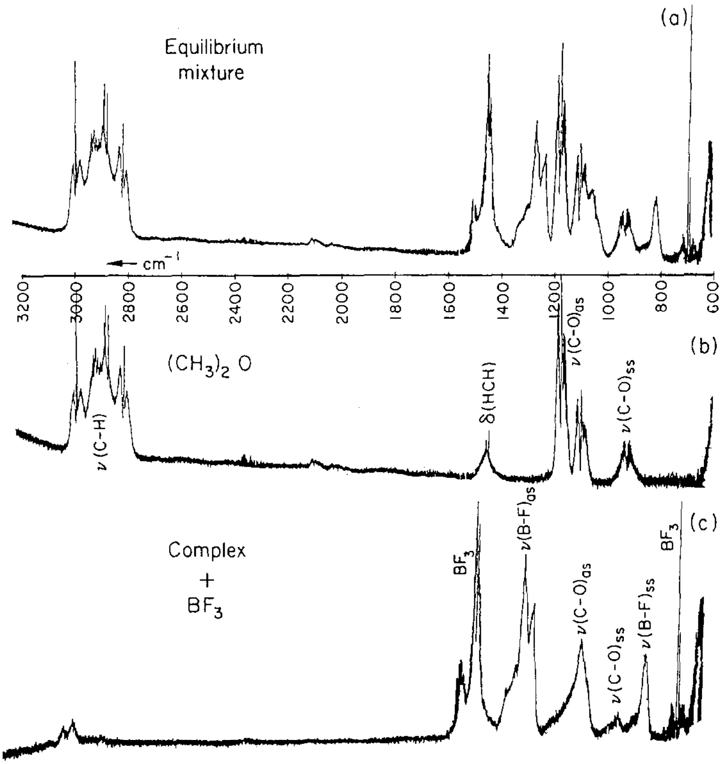

Fig. 1. FTIR spectra (a) of the complex in equilibrium with BF_3 and Me_2O (total pressure 2.2 torr at 297 K); (b) of the ether and (c) their difference spectrum, adjusted to eliminate absorption by Me_2O. The many sharp lines are due to uncompensated water vapor in the spectrometer. Spectrum (c) shows that the vibrational structure of the ether moiety is only slightly changed by complexing, in disagreement with the IR spectra published by Lascombe et al. [16].

the B–O distance is long, 1.719 Å). The spectra of the complex have been investigated [11]; the assigned frequency ν(O–B) $\approx 670\ cm^{-1}$.

EXPERIMENTAL

To measure the relaxation time of the ether:boron trifluoride system we used a T-jump configuration (Fig. 2). A pulsed Lumonics CO_2 laser ($\approx 1\ \mu s$ duration) was tuned to 957 cm^{-1} (the P(20) line of the 10.6 μ CO_2 band), which overlaps with the C–O symmetric stretching band in the free ether (quoted at 928 cm^{-1}) [12]. Rapid thermalization (Lambert and Salter [13] found from ultrasonic dispersion measurements that at 298 K dimethyl ether relaxes vibrationally in about 7 collisions) initiates the small increment in temperature ($3 < \Delta T < 6$). The consequent varying concentration of the complex was followed by measuring its absorption at 1057 cm^{-1}, currently assigned to the

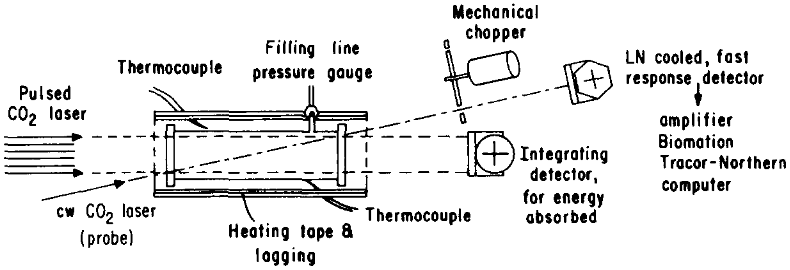

Fig. 2. Schematic of the experimental configuration. The chopper operates only during absorption calibration, in the absence of pulsed radiation.

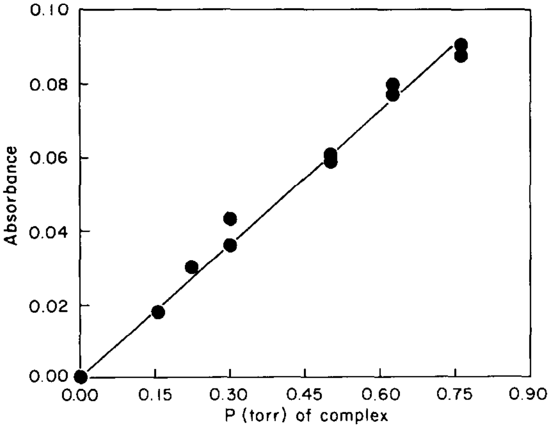

Fig. 3. The dependence of absorbance by the complex, at 1057 cm^{-1}, on its pressure.

C–O asymmetric stretching vibration (quoted at 1020 cm^{-1}) [11c], using a much weaker continuous wave Apollo laser (P(8) line of the 9.4 μ band). Absorption by the sample then returns to its pre-pulse value when the gas attains the cell wall temperature (≈ 10 ms). The sequence of measurements closely followed the protocol we developed in our study of the formic acid dimer/monomer system [7]. Similar experiments, based on the T-jump technique for following very fast gas phase relaxation times, have been carried out by Gozel [14] ($N_2O_4 \rightarrow 2NO_2$; *cis*→*trans*: 1,3-butadiene; and formic acid monomer/dimer). In contrast to Gozel [14] we estimated the rise in temperature directly by correlating the altered extent of absorption when the new equilibrium was reached at ≈ 40 μs, to that recorded for the same level of absorption under static conditions at the same total concentration of reagents. The dependence of absorption on the concentration of the complex is shown in Fig. 3. ($\log K_p(\mathrm{dis}) = -2983/T + 7.228$ (atm) [8c]; $\Delta H^0_{300} = 13.6 \pm 0.2$ kcal mol^{-1}; $\Delta S^0_{300} = 33.1 \pm 0.6$ e.u.).

Several significant precautions must be observed in performing these mea-

TABLE 1

Observed vs. calculated k^{uni} for dissociation

P_{mix} (torr)	P_{Ar} (torr)	T_{i} (K)	T_{f} (K)	$k_{\mathrm{d}}^{\mathrm{uni}}\times10^{-4}$ (s^{-1})	$k_{\mathrm{uni}}^{\mathrm{cal}}\times10^{-4}$ (s^{-1})	$k_{\mathrm{d}}^{\mathrm{bi}}\times10^{-11}$ ($\mathrm{mol}^{-1}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$)	
2.61	0.0	296.5	299.5	4.66 ± 1.03	4.73	3.30	
2.69	0.0	300.2	304.0	5.26 ± 0.57	5.74	3.66	
2.78	0.0	304.0	308.3	7.51 ± 0.55	6.89	5.12	
2.88	0.0	309.0	314.5	9.91 ± 0.77	8.76	6.63	
2.98	0.0	314.5	319.7	10.56 ± 1.17	10.56	6.95	
3.05	0.0	319.0	325.2	11.31 ± 1.12	12.73	7.38	
3.12	0.0	324.0	331.8	14.14 ± 1.87	15.71	9.16	
2.61	0.0	296.5	299.5	4.66 ± 1.03	4.73	3.30	low pressure
2.61	8.4	296.5	298.9	5.34 ± 0.57	6.15	3.78	range
2.61	30.4	296.5	301.5	11.20 ± 0.95	11.07	7.94	fall-off
2.61	59.4	296.5	300.7	12.70 ± 0.79	(16.3)		
2.61	117.4	296.5	299.5	15.00 ± 0.70	(26.42)		

surements. The cell windows were ZnSe; rock salt windows rapidly deteoriated over the areas that were irradiated by the laser, due to the development of a hazy coating of $NaBF_3Cl$. A considerable fraction of the incident energy ($\approx 30\%$) was absorbed by the two windows. The samples were prepared either by gas transfer to the cell from a reservoir of the pre-purified complex (liquid), or by injecting pre-set pressures of the individual acid/base components; no differences in kinetic data were noted. The cell was wrapped with heating tape and lagged; its wall temperatures were measured with several attached thermocouples. Incident pulse energies were ≈ 500 mJ, of which <20 mJ were absorbed by the sample, to generate temperature increments, which we assume were uniform along the beam path. The incident probe beam was reduced to <15 mW (we estimate that between 3.5 and 10.5 mW were incident on the sample). The cw laser was allowed to irradiate the cell contents until total equilibrium was attained with the wall temperature. However, so little probe-beam energy was absorbed that no change in the wall temperature could be detected after hours of irradiation. The liquid-nitrogen-cooled fast-response CdHgTe detector fed a low noise preamplifier in a shielded enclosure; then the signal was transferred to a differential amplifier-Biomation-Tracor-Northern (display) and ultimately to a computer. The recorded relaxation curves (64 pulses), though noisy, were well fitted by single exponential functions, from which relaxation times were evaluated. These ranged from 12 to 17 μs. Dissociation rate constants were calculated from

$$k_{\mathrm{uni}}^{-1}=\tau_{\mathrm{obs}}\left[1+\frac{p(\mathrm{A})+p(\mathrm{B})}{K_{\mathrm{diss}}^{p}}\right] \tag{2}$$

$$k_{\mathrm{bi}}=k_{\mathrm{uni}}/\{[\mathrm{A}]+[\mathrm{B}]+[\mathrm{C}]+0.1[\mathrm{Ar}]\} \tag{3}$$

The experimental results are summarized in Table 1. With regard to the dependence of the measured unimolecular association constant on the effective pressure we assumed that the collision efficiency of the added argon as a third body was 0.1 that of the ether. Larger pressures of the diluent could not be used because significantly above 100 torr the incident laser pulse set off acoustical oscillations that perturbed the relaxation curve. From Fig. 4 ($\ln k^{\rm uni}_{\rm diss}$ versus $\ln p_{\rm eff}$) it appears that the "knee" of the unimolecular fall-off curve occurs at about $P_{\rm eff} \approx 10$ torr; at lower pressures the system follows second order kinetics. An Arrhenius plot of $\ln k_{\rm uni}$ versus $1000/T$ is presented in Fig. 5. The least squares fitted value is $E_a = 6.1 \pm 0.8$ kcal mol^{-1}, which is somewhat less than half of the reported value of $\Delta H^0{}_{\rm diss}$. A typical association rate con-

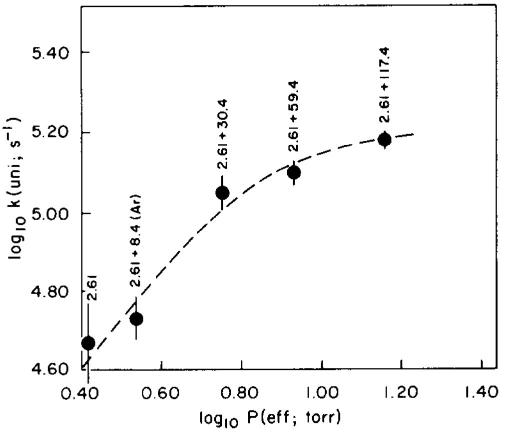

Fig. 4. The "fall-off" curve: $k^{\rm uni}_{\rm obs}$ vs. effective pressure ($\beta_{\rm Ar} = 0.1$); $T \approx 300$ K.

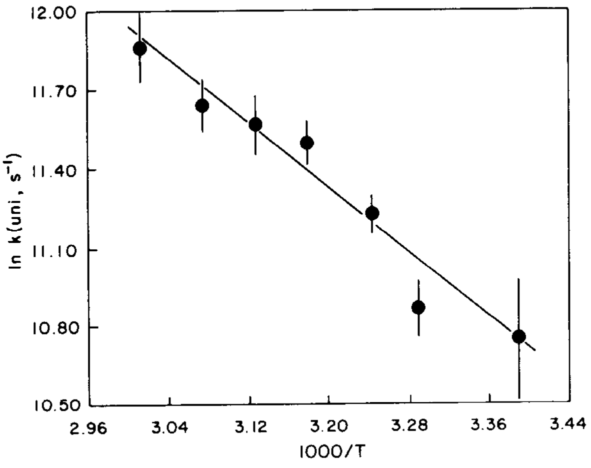

Fig. 5. Arrhenius plot of the unimolecular rate constant ($\beta_{\rm ether} = \beta_{\rm BF_3} = \beta_{\rm comp} = 1$) vs. relaxation temperature; $p({\rm Ar}) = 0$.

stant, derived by reflecting the unimolecular dissociation rate constant through the equilibrium constant, for mid-range, is 4×10^{11} mol^{-1} cm^3 s^{-1} (at 310 K). This is very close to the value reported by Kistiakowsky and Klots [3] for the association rate constant of boron trifluoride with methylamine, and is an order of magnitude smaller than the association rate constant of two alkyl radicals [15]. Hence the measured relaxation times for the $BF_3/O(CH_3)_2$ system are well within the expected range. As anticipated, k_{assoc} declines with increasing temperatures (6.21 at 300 K to 2.23×10^{11} at 332 K, fitted empirically to $(T/300)^{-10.2}$).

DISCUSSION

The low E_a was surprising. The displacement mechanism (1) is not acceptable since the dependence of k_{uni} on the Ar pressure (Fig. 4) is typical of unimolecular fall-off, and markedly unlike that found for the $(FA)_2 \leftrightharpoons 2FA$ relaxation rate. Furthermore, the observed discrepancy between ΔH^0_{300} and E_a is too large for such a process. There are no indicators of particularly weak coupling between the reaction coordinate (B–O bond stretching) and the other molecular oscillators. Note the activation energy was measured for a low pressure sample, in the second order regime (2.61–3.12 torr). The simplest assumption is to express k_{uni} in RRK form, with $\Delta E^0 = \Delta H^0 - RT$

$$k_{uni}^{(\text{low p limit})} = \omega\left[\frac{13000}{RT}\right]^{s-1}\frac{1}{(s-1)!}\exp\left[-\frac{13000}{RT}\right] \tag{4}$$

where $\omega \equiv Z_{CM}[M]$ is the collisional de-excitation frequency, and s is the effective degeneracy of the equivalent oscillator, generally estimated $s \approx C_{vib+int.rot.}/R$. The vibrational heat capacities of $(CH_3)_2O$ and BF_3 at 314 K (our midrange) are 10.3 and 6.3 cal mol^{-1} deg^{-1}, respectively; the six low frequencies developed by association contribute about 6 units. Hence $(s-1) \approx 10.4$. In Table 1, values for k^{cal}_{uni} were derived from eqn. (4), assuming $r = 2.4$ Å. As expected, the last two values are high because these pressures are within the knee of the fall-off region. One may write $E^{lpl}_{act} = \Delta E^0 - (s-3/2)RT = 7.5$ kcal mol^{-1}, somewhat higher than the directly measured value, but within the approximations inherent in this treatment.

Extrapolation of the log k_{uni} versus log p curve to high pressures indicates $k_{300} \approx (2.5\text{–}3.6)\ 10^5$ s^{-1}. When expressed in Arrhenius form, with $E_a = 13.0$ kcal, $A = (0.74\text{–}1.06)\ 10^{15}$ s^{-1} $= (ekT/h)\exp(\Delta S^{+}/R)$; hence, $\Delta S^{\dagger} \approx 8.2$ e.u. This is about 3 e.u. less than values found for typical bond fissions (≈ 11.5 e.u.), and indicates that the already weak B–O bond needs to undergo a small extension to reach the critical transition structure. An attempt to reduce these kinetic data via a standard RRKM program underscored the inapplicability of the tight binding model to this system. In the critical transition structure free rotation about the B–O bond was assumed, but the low four bending frequencies, treated as slightly anharmonic oscillators were clearly inappropriate.

This and similar kinetic systems merit more extensive investigations. An attempt should be made to minimize acoustical oscillations (cell design) and measurements made with more efficient collision partners so as to obtain rate constants and an activation energy at much higher pressures. Also a significant test for rapid thermal relaxation would be provided were kinetic relaxation times determined when other absorption bands are irradiated; in particular, if it were possible to use a source coincident with ν(B–O). Extension of this experiment to other bases (THF, thioethers, ketones) will provide interesting highlights on the relative degrees of coupling between the reaction coordinate and the other molecular oscillators.

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