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Thermal Decomposition of ClCN

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The thermal decomposition of cyanogen chloride was studied in a shock tube, using specific absorption spectroscopy to follow the concentration of CN radicals as a function of time behind the shock wave. This investigation is similar to the previously studied dissociation of cyanogen, but the kinetics are much more complex because of the possibility of reactions involving the unlike radicals CN and Cl.

A mechanism involving six reactions is proposed; these account for all features which characterize the observed results. Values for some ratios of rate constants have been obtained by direct analysis of the CN absorption curves. A method of trial curve fitting using a digital computer was used to deduce the absolute values of the rate constants for the important steps.

INTRODUCTION

THE heat of formation of CN is still subject to debate. Among the recent reports on this quantity, two shock-tube studies gave 99 and 109 kcal/mole[1,2]; mass-spectrometric investigations of cyanogen, cyanogen halides, and cyanoacetylenes led to 89 kcal/mole,[3] while a mass spectrometric analysis of the vapor in equilibrium with nitrogen and graphite at elevated temperatures gave 109 kcal/mole.[4] Of equal interest are the rates and activation energies of dissociation of C_2N_2 and XCN (X=halogens, $-C_2H$). In general, similarities between the characteristic features of the dissociation of the halogen diatoms and these compounds are to be anticipated[5]; the CN group behaves as a rigid unit but it possesses more degrees of freedom than does a mass point. Also at sufficiently high temperatures, the two CN's react to produce N_2+C_2. A shock-tube study of the pyrolysis of BrCN, in the temperature range 2500°–7000°K has been reported[6]; the kinetics was followed from the emission of characteristic radiation by CN and C_2.

This is a preliminary report on a shock-tube study of the dissociation of ClCN over the temperature range 2000°–2800°K, as followed by absorption at the (0, 0) band head of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ of CN (λ3883), using the technique developed for the study of the C_2N_2 dissociation.[1] Attempts were made to obtain both the $\Delta H^\circ_{\text{diss}}$ from equilibrium conditions far behind the shock front, and the kinetics of the process from the shock-front structure. In the former, we have not yet succeeded. The latter proved much more complicated than the analogous dissociation of C_2N_2 because of the relatively large number of reactions in which the products of the initial dissociation can participate.

EXPERIMENTAL

Cyanide chloride was obtained from the American Cyanamid Company. It was condensed at −78°C (dry ice–acetone) and pumped on to remove volatile impurities. Five percent and 0.5% mixtures were prepared with Matheson 99.998% argon, in 12-liter bulbs. These were allowed to stand overnight before use. Mass-spectrometric analysis showed that the small water peak initially present was removed by passing the argon through P_2O_5 before mixing.

The shock tube and associated equipment are shown schematically in Fig. 1. The tube was brass, $1\frac{1}{2}$-in. i.d.; scribed brass diaphragms were used. The concentration of the CN radical behind the shock was followed by means of specific absorption spectroscopy. Details of this method, and of the tube itself, have been given in our reports.[7] The source was a flash tube containing 10 mm butane, 3 mm nitrogen, and 15 mm argon. With 200 Ω resistance and sufficient inductance in series with the condenser bank, the emitted CN radiation pulse was substantially flat for 500–600 μsec. For nearly all this work the absorption intensity was measured at the (0–0) (3883 Å) band of the $B, {}^2\Sigma^+ \rightarrow X, {}^2\Sigma^+$ (ground state) of CN. A Jarrel–Ash 8200 monochromator with 25-μ entrance and exit slits was set for maximum signal from the flash tube. This corresponds to a bandwidth of 0.75 A at the head of the P branch and encompasses the lines from about $J=20$ to $J=37$. Incident shocks were run to produce temperatures in the range 2000°–2800°K. In addition to the CNCl–argon mixtures, some shocks were run with CNCl–

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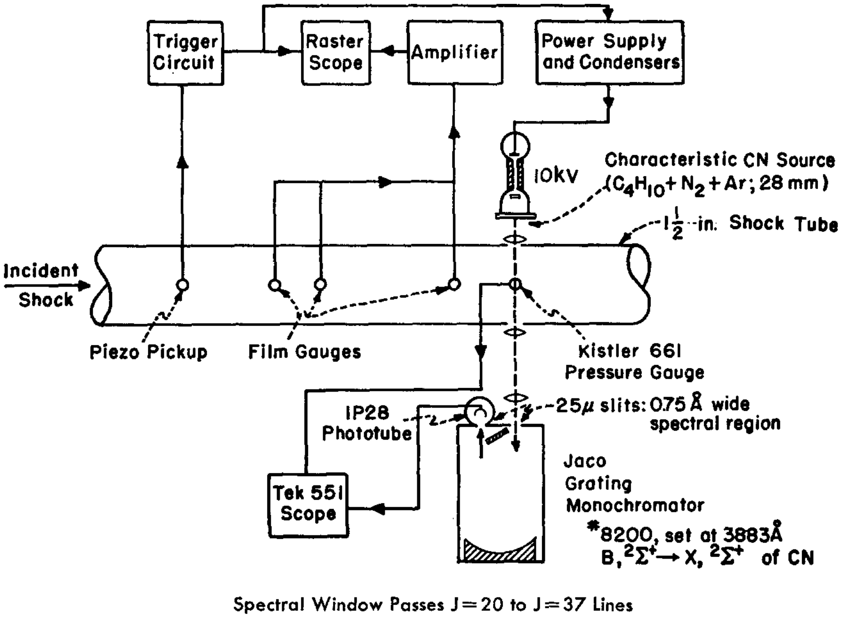

FIG. 1. Block diagram of apparatus.

Cl_2–argon mixtures, with CNCl:Cl_2=3:1. Further experimental details are summarized in Table I.

PROPOSED MECHANISM

The characteristic form of the curve for CN concentration as a function of time behind the shock is a fast initial rise, a flatter portion, and a final rise to the equilibrium value. This is shown in Fig. 2, Curve B. Under various conditions the initial region becomes too short (A) or too small (C) to be observed. To account for these curves the following six reactions, with their inverses, are postulated[8]:

$$\mathrm{CNCl+Ar}\underset{k_7}{\overset{k_1}{\rightleftharpoons}}\mathrm{CN+Cl+Ar}, \tag{a}$$

$$\mathrm{CN+CNCl}\underset{k_8}{\overset{k_2}{\rightleftharpoons}}\mathrm{C_2N_2+Cl}, \tag{b}$$

$$\mathrm{Cl+ClCN}\underset{k_9}{\overset{k_3}{\rightleftharpoons}}\mathrm{Cl_2+CN}, \tag{c}$$

$$\mathrm{C_2N_2+Ar}\underset{k_{10}}{\overset{k_4}{\rightleftharpoons}}\mathrm{2CN+Ar}, \tag{d}$$

$$\mathrm{Cl_2+Ar}\underset{k_{11}}{\overset{k_5}{\rightleftharpoons}}\mathrm{2Cl+Ar}, \tag{e}$$

$$\mathrm{2ClCN}\underset{k_{12}}{\overset{k_6}{\rightleftharpoons}}\mathrm{Cl_2+C_2N_2}. \tag{f}$$

The fast initial rise corresponds to the rapid production of CN in (a). This CN is used up in (b), which is very fast, so that a quasisteady state is reached. As more of the CNCl becomes converted to C_2N_2, (d) becomes important and [CN] finally rises to its equilibrium value.

The rate equations for the system may be written in somewhat simplified form for the case when only CNCl and argon are present initially. Then the concentrations are related by

$$[\mathrm{CNCl}]_{t=0}=[\mathrm{CNCl}]+[\mathrm{CN}]+2[\mathrm{C_2N_2}]$$
$$=[\mathrm{CNCl}]+[\mathrm{Cl}]+2[\mathrm{Cl_2}].$$

Call $[\mathrm{CNCl}]_{t=0}\equiv\phi$, and express all the concentrations relative to ϕ:

$$x=[\mathrm{CNCl}]/\phi,$$
$$y=[\mathrm{CN}]/\phi,$$
$$z=[\mathrm{Cl}]/\phi,$$
$$p=[\mathrm{C_2N_2}]/\phi=1-x-y,$$
$$q=[\mathrm{Cl_2}]/\phi=1-x-z.$$

Then

$$dx/dt=-C_1x-C_2xy-C_3xz-C_6x^2+C_7yz+C_8pz+C_9qy+C_{12}pq, \tag{1}$$

$$dy/dt=C_1x-C_2xy+C_3xz+C_4p-C_7yz+C_8pz-C_9qy-C_{10}y^2, \tag{2}$$

$$dz/dt=C_1x+C_2xy-C_3xz+C_5g-C_7yz-C_8pz+C_9qy-C_{11}z^2, \tag{3}$$

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[8] The reaction $2CN\rightarrow C_2+N_2$ was not included because during the early times, for low temperature, and hence low [CN], its contribution is presumed to be small.

TABLE I. Experimental conditions for typical runs.

0.5% C_2N_2 in Ar (full set: from No. 250 to No. 273).

Run No.	p_1 (mm Hg) at 300°K	u_i (mm/μsec)	T_2 (°K)	ρ_2/ρ_1
250	24.	1.543	2394	3.58
253	33.	1.516	2320	3.55
254	32.	1.569	2467	3.59
255	33.	1.523	2337	3.56
256	30.	1.602	2562	3.60
260	12.	1.645	2683	3.62
261	7.5	1.642	2675	3.62
266	7.5	1.681	2793	3.64
270	11.	1.598	2550	3.60
272	50.	1.567	2462	3.59
273	53.	1.537	2377	3.57

5.0% C_2N_2 in Ar (full set: 238, 239, and 279–293)

	p_1 (mm Hg) at 300°K	u_i (mm/μsec)	T_2(°K) (no reaction)	T_2(°K) (equil)	ρ_2/ρ_1 (n.r.)	ρ_2/ρ_1 (equil)
238	25	1.564	2370	2175	3.91	4.32
280	20	1.610	2500	2275	3.94	4.38
293	17	1.509	2225	2050	3.88	4.27

Runs 332–340 used 0.5% CNCl and 0.17% Cl_2 in Ar.

Temperature range 2320° to 2712°K.

where

$$C_1=k_1[\mathrm{Ar}] \qquad C_7=k_7[\mathrm{Ar}]\phi;$$
$$C_2=k_2\phi \qquad C_8=k_8\phi;$$
$$C_3=k_3\phi \qquad C_9=k_9\phi;$$
$$C_4=2k_4[\mathrm{Ar}] \qquad C_{10}=2k_{10}\phi[\mathrm{Ar}];$$
$$C_5=2k_5[\mathrm{Ar}] \qquad C_{11}=2k_{11}\phi[\mathrm{Ar}];$$
$$C_6=2k_6\phi \qquad C_{12}=2k_{12}\phi.$$

At $t=0$, $x=1$ and all the other concentrations (except [Ar]) are zero. These equations were programmed for solution on a Burroughs No. 220 digital computer using the Runge–Kutta method. Initial time intervals of 1 μsec were used; this was found to be adequate for the first 10 μsec. The interval was increased progressively, the later values being found individually by solving in decreasing steps: typically 20 μsec.

APPROXIMATE SOLUTIONS FOR SHORT TIMES

For the initial period there is an approximate analytic solution. Taking the forward reactions (a) and (b) alone, and neglecting the depletion of CNCl

$$[\mathrm{CN}]=[\mathrm{Ar}](k_1/k_2)[1-\exp(-k_2\phi t)]. \qquad (4)$$

This shows how the CN reaches a *steady-state* concentration of $k_1[\mathrm{Ar}]/k_2$. [Fig. 3(a)]. In the next approximation include also the forward reaction (d); (b) is so rapid that, except during the initial fast rise, nearly all the CN formed in (a) ends up as C_2N_2. Thus neglecting CNCl depletion, $[C_2N_2]\approx k_1[\mathrm{Ar}]\phi t$. This will overestimate $[C_2N_2]$ when t is small, but $[C_2N_2]$ is itself small under these conditions. Hence [Fig. 3(b)]

$$[\mathrm{CN}]=\frac{k_1[\mathrm{Ar}]}{k_2}\left[1+\frac{2k_4[\mathrm{Ar}]}{k_2\phi}(k_2\phi t-1)-\left(1-\frac{2k_4[\mathrm{Ar}]}{k_2\phi}\right)\exp(-k_2\phi t)\right]. \qquad (5)$$

Comparison with machine calculations shows that this is a good approximation for the initial period (Fig. 4), assuming the mechanism proposed above.

From the above expression three quantities may be extracted, based on the initial portion of the experimental curve [see Fig. 3(b)]:

(i) The time at which the linear term starts to dominate the exponential term in (5). This occurs

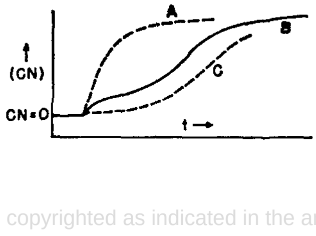

FIG. 2. Typical observed form of CN concentrations behind the shock wave.

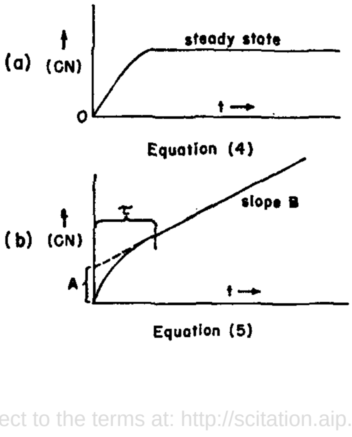

FIG. 3. Initial approximations: (a) Eq. (4); (b) Eq. (5).

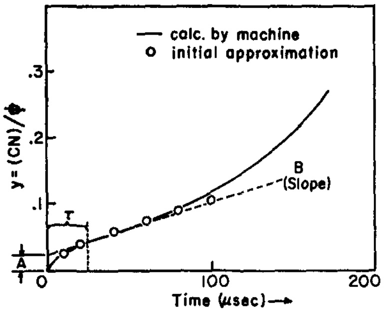

FIG. 4. Comparison of estimate based on initial approximation and the magnitude of y calculated by machine program.

when $e^{\alpha}=(\alpha/400\gamma)-1$; $\alpha\equiv k_2\phi t$; $\gamma\equiv k_4\phi t$ and $\mathrm{Ar}/\phi=200$. (A plot of γ vs α permits one to read γ for each ϕ and t, using our previous value for k_4, and thus to deduce k_2.)

(ii) the value of [CN] at $t=0$, obtained by projecting backwards the linear portion of the curve. Call this A.

(iii) the slope of the linear portion. Call this B. From (5) we see that

$$A=(k_1[\mathrm{Ar}]/k_2)-(2k_1k_4[\mathrm{Ar}]^2/k_2^2\phi), \qquad (6)$$

$$B=(2k_1k_4[\mathrm{Ar}]^2/k_2)+\text{small time dependence.} \qquad (7)$$

THERMOCHEMISTRY

In order to relate the observed shock velocity to temperature and composition of the gas, it is necessary to know the enthalpies of the species present. The values used are summarized in Table II. The species considered are Ar, CNCl, CN, Cl, C_2N_2, Cl_2, C_2, and N_2. Shock temperatures were calculated for the case of no reaction, and for various equilibrium conditions involving some or all of the above species. The equilibrium constants were formed from the free energies, and are listed in Table III. All the thermochemical quantities were obtained from JANAF thermochemical tables except the heat of formation of CN. As some doubt exists as to the value of this quantity, five values ranging from 91.2 to 109.4 kcal/mole were used. All the kinetic analyses are based on the value 99.4, which make the dissociation energy of cyanogen 125 kcal/mole.[1] The similar analyses based on the other four values have yet to be completed.

TABLE II. ΔH° for Reactions (a)–(f) at 2000° and 2800°K, in kcal/mole, assuming $\Delta H^{\circ}_{\mathrm{form}}[\mathrm{CN}]=99.4$.

	(a)	(b)	(c)	(d)	(e)	(f)
$\Delta H_{2000°}$	96.73	−26.42	36.15	123.15	60.58	9.73
$\Delta H_{2800°}$	96.64	−25.39	35.32	122.03	61.32	9.93

ABSORPTION COEFFICIENT OF CN

The absorption coefficient for CN was found by comparing the observed absorption, when the CN had reached equilibrium, with the calculated equilibrium concentration appropriate to the observed shock velocity. In these equilibria the species considered were Ar, CNCl, CN, Cl, C_2N_2, and Cl_2. The CN absorption remained flat after equilibrium was reached. The results (Fig. 5) are rather scattered, because the absorption is large, and a small error on the oscilloscope trace introduces a large error in the absorption coefficient. It was not possible to reduce either the density or temperature, because the testing time (400 μsec) would have been too short to permit the attainment of equilibrium. Most of the points are for 5% CNCl–argon, for this reason, though most of the kinetic analysis is based on ½% CNCl–argon.

Emission from the shocked gas was negligible compared with that from the source (this was shown experimentally). Hence,

$$(\mathrm{CN})=\mu\ln(I_0/I), \qquad (8)$$

with $\mu=2.27\times10^{-6}$, when [CN] is measured in moles per liter. This is about twice the value found previously,[1] from the dissociation of C_2N_2, using a similar setup (1.15×10^{-6}).

ANALYSIS OF DATA

Initial Period

The experimental curves give the transmitted intensity ratio vs time, in laboratory coordinates. One must then deduce the quantities A, B [see Fig. 3(b) and Eqs. (6), (7)] from these curves. If the total absorption is small, so that [cf. Eq. (8)],

$$(I_0-I)\approx\mu I_0(\mathrm{CN})=\mu I_0 y\phi, \qquad (9)$$

intercepts and slopes (A' and B') may be directly

TABLE III. Equilibrium consts. K_c for reactions (a)–(f) assuming $\Delta H_f[\mathrm{CN}]=99.4$ kcal/mole. Units: moles per liter.

T (°K)	$\log_{10}K_c$ (a)	(b)	(c)	(d)	(e)	(f)
2000	−5.847	1.969	−3.375	−7.816	−2.471	−1.406
2200	−4.930	1.709	−3.020	−6.640	−1.911	−1.311
2400	−3.834	1.400	−2.593	−5.234	−1.240	−1.193
2600	−2.978	1.160	−2.262	−4.138	−0.716	−1.101

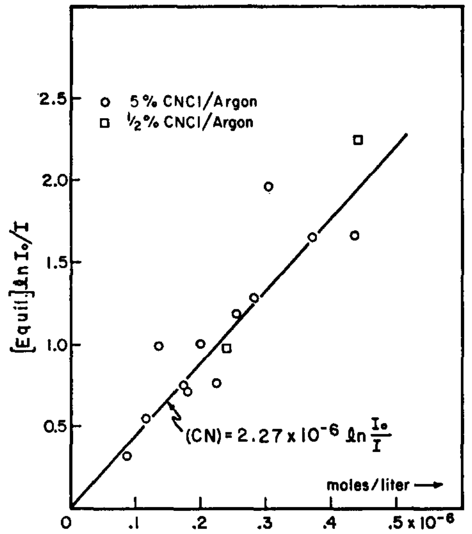

FIG. 5. Measured absorption coefficient, as deduced for various concentrations of CN; $(\mu l)_{\text{Av}}$ is essentially independent of T; l (optical path length) $=3.81$ cm. Equilibrium levels of [CN] were calculated for $\Delta H_{f0}°[\text{CN}]=99.4$ kcal/mole.

estimated from the oscilloscope traces

$$A'=A\mu I_0 \tag{10}$$

$$B'=B\mu I_0(\rho_2/\rho_1), \tag{11}$$

where the factor (μI_0) converts [CN] to I, and the density ratio ρ_2/ρ_1 converts t_{lab} to the kinetic (particle flow) time. On neglecting the second term in (6), i.e., in $[\text{Ar}]^2$,

$$A\approx k_1[\text{Ar}]/k_2.$$

Figure 6 shows a plot of log (A/ϕ) vs $1/T$ for some $\frac{1}{2}\%$ CNCl shocks for which $A/\phi\approx 200k_1/k_2$. In theory k_2 can be found from the time taken for a quasisteady-state concentration to appear. However, these results show a large scatter, (Fig. 7), as they are based on a very small portion of the oscilloscope trace.

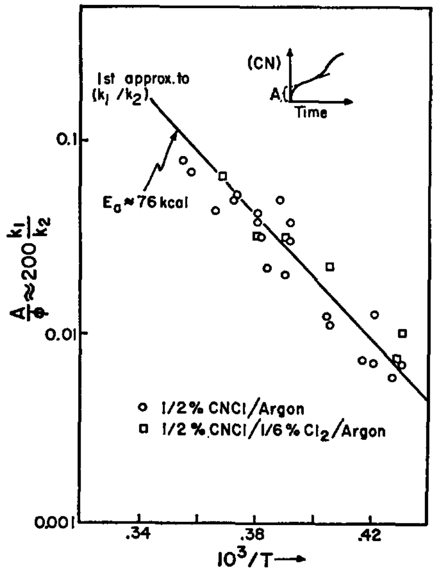

FIG. 6. Analysis of initial stages (intercept vs $10^3/T$).

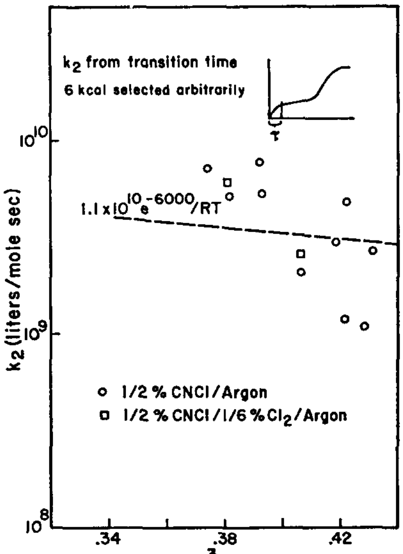

FIG. 7. Analysis of initial stages (transition period vs $10^3/T$).

The activation energy of Reaction (b) must be low (cf. Table II). A value of 6 kcal was selected and a line drawn through the points of Fig. 7. With this value for k_2, and the above approximation for (k_1/k_2), the values of B can be used to derive k_4. The points are shown on Fig. 8. Finally, from k_4 and k_2, k_1 may be calculated based on the experimental values of A, on the basis of the exact formula (6). The points are shown in Fig. 9. These results are more consistent than are the points plotted in Fig. 6 because of the inclusion of the second term in Eq. (6).

Curve Fitting

The above procedure gave suitable initial trial values for k_1, k_2, and k_4. Then k_3, k_5, and k_6 were estimated and trial calculations run on a digital computer. The rate constants were assumed to have the form $A\exp(-E/RT)$, with magnitudes for the parameters indicated as "First Trial," listed in Table IV. The calculated curves (a) are shown, superimposed on the experimental results, in Fig. 10. On the whole they rise too rapidly. Hence, a second trial fit was made (b) with a reduced value for the pre-exponential factor of k_4 (cyanogen dissociation rate).

TABLE IV. Parameters used in curve fitting. Rate constants are of form $k=A\exp(-E/RT)$.

Curve fit	(i)	(ii)	(iii)	E
$\log_{10}A$ (1)	13.53	13.53	13.53	91.5
$\log_{10}A$ (2)	10.05	10.05	10.05	6
$\log_{10}A$ (3)	10	10	11	34
$\log_{10}A$ (4)	14.61	14.3	14.23	100.4
$\log_{10}A$ (5)	10	10	10	40.6
$\log_{10}A$ (6)	10	10	10	60

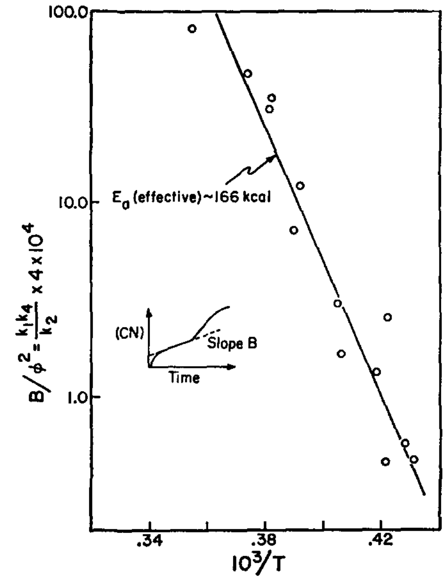

FIG. 8. Analysis of initial stages (slope B vs $10^3/T$).

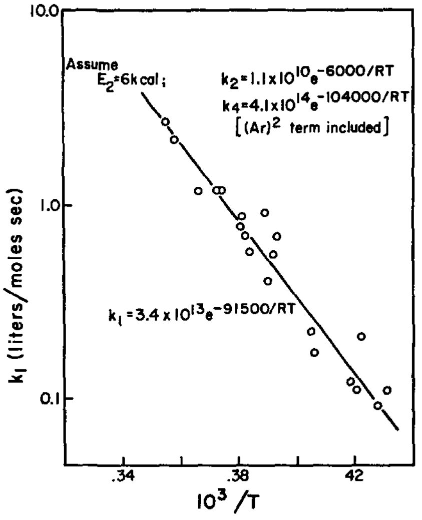

FIG. 9. k_1 from initial analysis vs $10^3/T$.

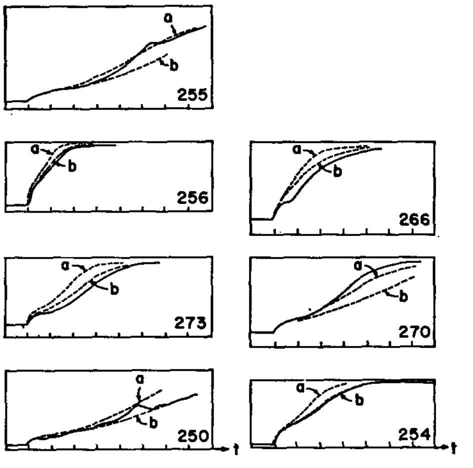

FIG. 10. Results of curve fitting: CN concentration vs time (40 μsec/div). —— Experiment; (a) First trial; decrease $k_4(A_4)$; (b) Second trial; decrease $k_4(A_4)$; increase $k_3(A_3)$.

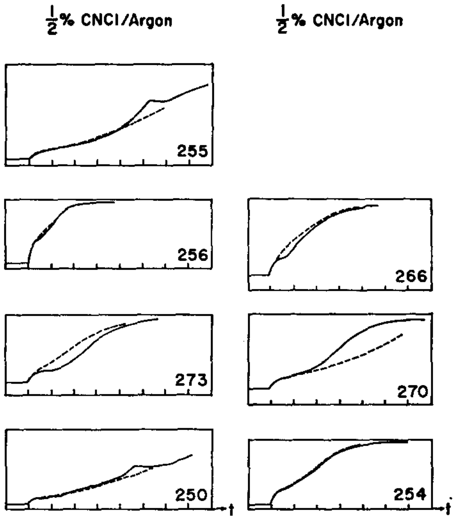

FIG. 11. Third trial in curve fitting: CN concentration vs time (40 μsec/div). ——, experiment; – – –, calculation.

A third set of curves computed with slightly adjusted values, is shown in Figs. 11, and 12, left. Increasing k_3 makes the slow-rising curves faster without altering the rapid ones. However, the curves are fairly insensitive to variations in k_3. Reaction (f) is too slow to be important.

The dissociation of chlorine, Reaction (e), is certainly faster than the k_5 used. However, the main supply of Cl atoms is Reaction (b), and the equilibrium lies well over to dissociated side; the process $Cl_2 \rightarrow 2Cl$ is not significant in the mechanism. Introducing a much larger k_5, would require that the integration be performed with much smaller steps.

Several curve fits for 5% CNCl–Ar mixtures are given in Fig. 12, right. For this concentration there is

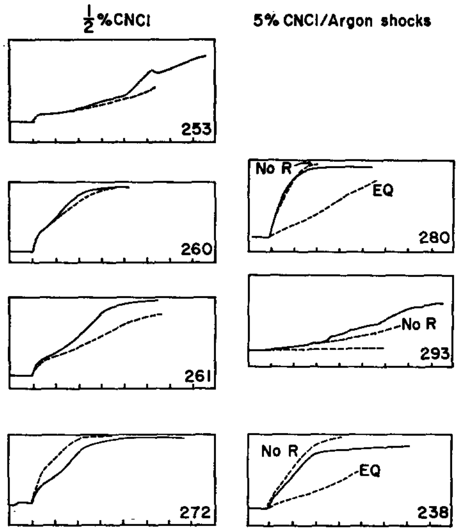

FIG. 12. More curve fitting (third trial): (left) $\frac{1}{2}$% CNCl (40 μsec/div); (right) 5% CNCl (40 μsec/div for No. 280. 293; 50 μsec/div for 238). In 5% runs: – – – (upper): calculated for initial temp (no reaction); – – – (lower): calculated for equilibrium temperature; —— experiment. The large increment in temperatures is due to dissociation.

a larger temperature change caused by the reaction. Kinetic curves are shown computed for the "no-reaction" and the "equilibrium" temperatures. The former give much better fits, as would be expected.

CONCLUSIONS

Although the reaction is too complex to analyze completely, the mechanism given, together with reasonable rate constants, is capable of representing the shape and variation of the observed cyanogen concentration with time. The ratio of rates (a) and (b)

$$\mathrm{CNCl+Ar=CN+Cl+Ar}, \qquad \text{(a)}$$

$$\mathrm{CNCl+CN=C_2N_2+Cl}, \qquad \text{(b)}$$

has been found directly to be

$$k_1/k_2=3.1\times10^3\exp(-85\,500/RT),$$

k_2 has been placed as to its order of magnitude (Fig. 8). The best fits for the observed curve were computed with a value for the dissociation rate constant for C_2N_2 of $10^{14.23}\exp(-100\,400/RT)$ liter/mole·sec which is almost identical with that reported previously.[1] These rates lead indirectly to a value for $(\mathrm{CNCl+Ar\rightarrow CN+Cl+Ar})$ of $k_1=10^{13.53}\exp(-91\,500/RT)$ liter/mole·sec.

ACKNOWLEDGMENT

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Barrier Studies in the Halopropenes. I. The Microwave Spectrum, Barrier to Internal Rotation, Quadrupole Coupling Constants, and Microwave Double-Resonance Spectra of 2-Chloropropene

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The microwave spectra of $CH_3C^{35}Cl{:}CH_2$ and $CH_3C^{37}Cl{:}CH_2$ have been observed in the ground and first excited torsional states. The ground-state rotational constants of $CH_3C^{35}Cl{:}CH_2$ are $A=9272.79\pm0.10$ Mc/sec, $B=4983.84\pm0.10$ Mc/sec, and $C=3304.39\pm0.10$ Mc/sec. The ground-state rotational constants for $CH_3C^{37}Cl{:}CH_2$ are $A=9272.31\pm0.10$ Mc/sec, $B=4850.48\pm0.10$ Mc/sec, and $C=3245.11\pm0.10$ Mc/sec. The quadrupole coupling constants along the appropriate principal inertial axes in the ground torsional state of $CH_3C^{35}Cl{:}CH_2$ are $\chi_{aa}=-68.15\pm0.10$ Mc/sec, $\chi_{bb}=37.11\pm0.10$ Mc/sec, and $\chi_{cc}=31.04\pm0.10$ Mc/sec. The quadrupole coupling constants for $CH_3C^{35}Cl{:}CH_2$ in the excited torsional state were within the experimental error of the corresponding ground-state values. The quadrupole coupling constants in $CH_3C^{37}Cl{:}CH_2$ are $\chi_{aa}=-53.80\pm0.10$ Mc/sec, $\chi_{bb}=29.30\pm0.10$ Mc/sec, and $\chi_{cc}=24.50\pm0.10$ Mc/sec. Analysis of the first excited-torsional-state rotational spectrum yielded a barrier to the internal rotation of the methyl group of 2671±20 cal/mole.

Microwave double-resonance experiments were used to provide a positive confirmation for the assignments of the $0_{00}\rightarrow1_{01}$ and $1_{01}\rightarrow2_{02}$ transitions in $CH_3C^{35}Cl{:}CH_2$ as well as exhibiting some interesting features in the energy levels involved in the transitions. Two types of experiments were performed. The first experiments involved irradiating the quadrupole components in the $0_{00}\rightarrow1_{01}$ transition while observing the $1_{01}\rightarrow2_{02}$ transition. The second set of experiments involved irradiating one of the quadrupole components in the $0_{00}\rightarrow1_{01}$ transition and using a second klystron to observe the entire $0_{00}\rightarrow1_{01}$ triplet.

I. INTRODUCTION

It is believed that a careful study of the barrier to internal rotation in a system of controlled compounds such as in the mono- and disubstituted halopropenes may lend some insight into the origin of the barrier in these and other molecules. Since the barrier to rotation of the methyl group of all the molecules in the monosubstituted one- and two-fluoro- and chloropropenes, except 2-chloropropene, had been determined, we have investigated the microwave spectrum of 2-chloropropene primarily to measure the methyl group barrier.

Presently, the barriers appear not to be caused solely by steric effects, but are also dependent on the axial bond properties of the molecules.[1–3] The halopropenes provide a controlled system of molecules in which one may be able to establish both the effects of the steric interactions on the barrier as well as effects due to the actual bonding properties of the molecule. The first apparent steric effect in these molecules was the lower-

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