sure effect. A series of runs was made at a temperature of 385°, keeping the HCl pressure constant for each run, but changing it between runs. The rate constant, k, is 21×10^{-19} (moles cm.$^{-2}$)^2 sec.$^{-1}$ at 500 mm., 16.5×10^{-19} at 100 mm., and 14.5×10^{-19} at 30 mm. Thus a 17-fold increase in pressure increases the constant by only about 45%. In Fig. 3, the value of the rate constant, k, is plotted against the HCl pressure. It will be noted that with increasing pressure the rate appears to be approaching a steady value. At the lower pressures, the small initial rapid reaction is less pronounced.

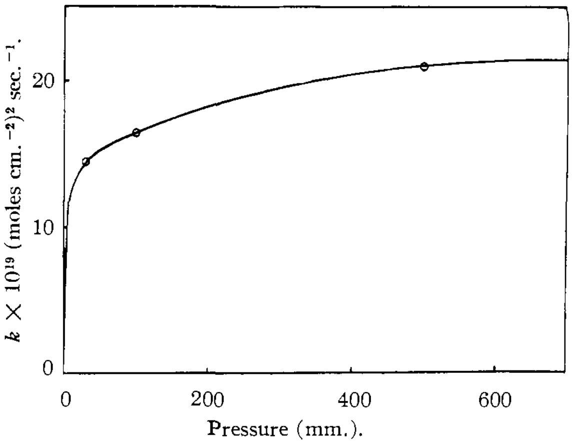

Fig. 3.—Variation of the specific reaction rate constant with HCl pressure.

Conclusions

Although the kinetics of the reaction of HCl with Pyrex indicate that the rate-determining step involves a diffusion process through the glass, the identity of the diffusing substance has not been established. There are three distinct possibilities: (1) HCl may be diffusing from the surface to the interior, (2) Na_2O (*i.e.*, sodium ions accompanied by an equivalent number of oxide ions) may be diffusing from the interior to the surface, or (3) HCl may dissolve in a layer of adsorbed water on the surface of the glass fibers, followed by a counter diffusion of H^+ ions into the glass and Na^+ ions to the surface.[5] Considering the temperature range in which the reaction is observed, the last of these possibilities seems most likely.

Several studies of halogen isotope exchange reactions using hydrogen halides have been made in Pyrex vessels.[2,3] In such cases the formation of sodium halide on the reaction vessel surface may play an important role in the mechanism of exchange. Since Na_2O tends to migrate to the surface when glass is heated,[6] glassware which has been exposed to glassblowing operations might be expected to have a higher surface concentration of Na_2O than do the fibers studied in this work.

AUSTIN, TEXAS

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[5] R. W. Douglas and J. O. Isard, *J. Soc. Glass Tech.*, **33**, 289T (1949).

[6] H. S. Williams and W. A. Weyl, *Glass Ind.*, **26**, 275 (1945).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

Energy Transfer Processes in the Unimolecular Decomposition of Nitryl Chloride[1]

BY MILTON VOLPE AND HAROLD S. JOHNSTON

RECEIVED MARCH 23, 1956

The decomposition of nitryl chloride has been studied at 203° in the presence of each of 16 foreign gases at total pressures between 3 and 9 mm. As shown previously[2] the rate under such conditions is the rate of activation of nitryl chloride by collision. This paper lists relative rate constants for activation by the various foreign gases as well as the relative efficiency of energy transfer, collision per collision. As noted before,[2-4] deactivation does *not* occur upon every collision. The relative efficiency of energy transfer shows several strong empirical correlations with molecular interaction parameters such as boiling point and the constants from the Lennard-Jones potential function, and gases with permanent dipole moments are all more efficient than comparable non-polar molecules. On the other hand these results indicate, somewhat surprisingly, very little or no correlation with the number of atoms or the number of oscillators in the foreign gas.

Schumacher and Sprenger[5] studied the decomposition of nitryl chloride and proposed the mechanism

$$NO_2Cl = NO_2 + Cl \qquad (1)$$

$$NO_2Cl + Cl = NO_2 + Cl_2 \qquad (2)$$

Thus they proposed their observed rate to be twice that of the elementary unimolecular decomposition. Our recent reinvestigation[2] confirmed all of these features and also demonstrated that the unimolecular reaction was essentially within its second-order region below 5 mm. Therefore the observed rate of reaction is the rate of activation according to the Lindemann[6] mechanism

$$\begin{aligned} A + M &\xrightarrow{a_{mi}} A_i^* + M \qquad (3) \\ A_i^* + M &\xrightarrow{b_{mi}} A + M \\ A_i^* &\xrightarrow{c_i} \text{products} \end{aligned}$$

where * denotes internal energy above the critical energy, i denotes some activated state of the reac-

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[1] Presented at the 128th meeting of the American Chemical Society, Minneapolis, Minn., Sept., 1955. Submitted to Stanford University in partial fulfillment of the requirements for the Ph.D. degree 1956.

[2] H. F. Cordes and H. S. Johnston, THIS JOURNAL, **76**, 4264 (1954).

[3] D. J. Wilson and H. S. Johnston, *ibid.*, **75**, 5763 (1953).

[4] H. S. Johnston, *ibid.*, **75**, 1567 (1953).

[5] H. J. Schumacher and G. Sprenger, *Z. Elektrochem.*, **35**, 653 (1929); *Z. physik. Chem.*, **B12**, 115 (1931). H. J. Schumacher, "Chemische Gas Reactionen," Edward Bros., Inc., Ann Arbor, Mich., 1943 (Photolithoprint reproduction), pp. 127–130.

[6] F. A. Lindemann, *Trans. Faraday Soc.*, **17**, 598 (1922).

tant A, M denotes the foreign gas, and the subscript m denotes possible dependence of the rate constant functions on the *identity* of M. The functions a_{mi} and b_{mi} have been averaged over all states of A and M, but the function c_i is a purely mechanical, not averaged, quantity.[7] At low pressures the observed rate is $\sum_{m}\Sigma_i a_{mi}\,[A]\,[M] = \sum_{m} a_m[A]\,[M]$; when A and M are both present in comparable amounts, the rate is $a_A[A][A] + a_m[A][M]$. By holding an initial reactant constant over a series of runs and varying [M], one can obtain a plot of observed k = rate/[A] against [M], and the slope is a_m and the intercept $a_A[A]_0$. The ratio a_m/a_A is written R_m and is referred to as the relative rate constant for activation, or by virtue of microscopic reversibility as the relative rate constant for deactivation.[4] Of greater interest than these relative rate constants, R_m, are the relative efficiencies "Collision per Collision," ρ_m, which have been described previously[3] as

$$\rho = R(\mu_{mA}/\mu_{AA})^{1/2}(\sigma_{AA}/\sigma_{mA})^2 \qquad (4)$$

where μ are reduced masses and σ are kinetic collision diameters (R and ρ obtained in the second-order region are not necessarily identical with the similar quantities obtained in the "fall-off" region as defined by Schumacher[5] and Trotman-Dickenson[8]).

Thus this reaction is ideal for a study of the effect of the type of foreign gas upon the relative efficiency of energy transfer. In this study a series of runs has been made at one temperature, 203°, with a constant low pressure of reactant, and with foreign gas pressures varied from 0 to about 6 mm.; under these conditions the decomposition was always within the second-order region. In this way relative efficiencies for energy transfer were obtained for the noble gases, five diatomic gases, three triatomic gases and four polyatomic gases, including the reactant and both final products.

Experimental

Apparatus.—The 50-liter reaction bulb and air thermostat used by Cordes[2] were adapted for the present study. Temperature was regulated by a phase-shift thyratron controller and was measured by three calibrated chromel-alumel thermocouples located at different positions over the surface of the reaction flask. During each run the temperature was constant to ±0.1° and uniform over the bulb to ±3/4°; over the entire series of runs the temperature remained between 476.0 and 477.4°K., and all rate constants were converted to 476.5°K. using Cordes[2] energy of activation. The gas-pipet system was re-designed in order rapidly and reproducibly to fill the reaction bulb with a series of mixtures, each containing identical concentrations of nitryl chloride but different concentrations of foreign gas. The degree of advancement of the reaction was determined by colorimetric (436 mμ mercury line) measurement of the concentration of nitrogen dioxide produced; calibration of nitrogen dioxide was carried out at 200° in the usual way. Stopcocks were lubricated with polytrifluorochloroethylene grease (Halocarbon).

Materials.—Silicon tetrafluoride was prepared by heating dry barium fluorosilicate ($BaSiF_6$) in a Pyrex tube, condensed in a liquid nitrogen cooled trap, and fractionated. The noble gases, helium, neon, argon, krypton and xenon, were Matheson's "reagent gases of highest purity" obtained in sealed glass bulbs. Hydrogen, nitrogen, oxygen and hydrogen chloride were obtained from commercial tanks and were passed through liquid nitrogen traps. Chlorine, nitrogen dioxide, carbon dioxide, nitrous oxide, sulfur hexafluoride and dichlorodifluoromethane were obtained from commercial tanks and were fractionated by bulb-to-bulb vacuum distillation before use.

Nitryl chloride was prepared by the method of Wise and Volpe.[9] Anhydrous hydrogen chloride gas was passed as a stream of fine bubbles through a porous glass disk and through a solution of nitric acid in sulfuric acid. A mixture of 50 cc. of 90% nitric acid, 120 cc. of 95% sulfuric acid and 130 cc. of 30% fuming sulfuric acid yielded about 50 cc. of crude nitryl chloride containing about 20% chlorine. Apparently nitryl chloride and chlorine form an azeotropic mixture, and ordinary fractionation did not completely separate them. However, almost all of the chlorine could be removed by vacuum distillation from −95° to a liquid nitrogen trap, and up to 30 cc. of purified nitryl chloride could be obtained from the solutions given above. The reaction between hydrogen chloride and the acid had to be stopped when the calculated yield was about 50% of theoretical in order to prevent contamination with nitrosyl chloride.

According to Wise and Volpe[9] the preparation of nitryl chloride takes place by the reactions

$$HNO_3 + 2H_2SO_4 \rightleftarrows NO_2^+ + H_3O^+ + 2HSO_4^-$$

$$NO_2^+ + HSO_4^- + HCl \longrightarrow NO_2Cl + H_2SO_4$$

while the production of chlorine could result from

$$NO_2^+ + HSO_4^- + 2HCl \longrightarrow Cl_2 + NOHSO_4 + H_2O$$

When the concentration of nitrosyl sulfuric acid becomes large enough, nitrosyl chloride is produced by

$$NOHSO_4 + HCl \longrightarrow NOCl + H_2SO_4$$

The purity of the nitryl chloride was tested by several different methods. Infrared absorption spectra demonstrated the absence of impurities such as nitrosyl chloride, nitrogen dioxide, nitric acid and hydrogen chloride. Ultraviolet absorption measurements set an upper limit on the amount of chlorine which could be present (less than 10%). The amount of nitrogen dioxide produced when the reaction was allowed to go to completion (12 half-lives) may be regarded either as confirming the stoichiometry

$$2NO_2Cl = 2NO_2 + Cl_2 \qquad (5)$$

or as a criterion of purity of the reactant. If the latter view is taken, the measurements indicated a purity of 98 ± 2%. A quartz spiral gas density balance was used to determine the purity of reactant and the second virial coefficient, indicating a purity of 96 ± 3%. Also chemical analyses were carried out. A known quantity of gas was added to excess standardized sodium hydroxide solution, the excess alkali was back titrated with acid, and chloride ion was determined gravimetrically. Qualitative spot tests showed that nitryl chloride reacted with base to produce, in part, nitrite and hypochlorite, which reacted with each other upon neutralization to form nitrate and chloride. This method of analysis indicated a purity of 99 ± 1%. The same purity was found for nitryl chloride prepared from nitrogen pentoxide and nitrosyl chloride[2]; the present method, however, is much simpler and faster.

Procedure during a Run.—The basic data, from which the relative efficiency of each foreign gas was calculated, consisted of a set of first-order rate constants for 10 to 20 different concentrations for each foreign gas (except xenon); in addition 3 or 4 blank runs with nitryl chloride alone were included in each set. The rate constants were obtained in the following manner: the pipets were filled, furnace temperatures were taken, and initial intensity I_0 of light passing through the evacuated bulb was measured. The reactant pipet was opened to the reaction flask for 10 seconds and then closed. The foreign gas was admitted to the reaction bulb, and light intensity I was taken every 10 seconds for 240 seconds or longer for some cases. The reaction bulb was pumped out and I_0 checked, it being found to hold constant (better than 0.5%) for these periods of 10 to 15 minutes. The concentrations of nitrogen dioxide and nitryl chloride were calculated in the usual way. A plot was made of log $[NO_2Cl]$ against time, the runs typically covered between $^1/_4$ and $^1/_2$ life, the slope of the line was taken from the graph,

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(7) H. S. Johnston, *J. Chem. Phys.*, **20**, 1103 (1952).

(8) A. F. Trotman-Dickenson, "Gas Kinetics," Academic Press, Inc., New York, N. Y., 1955, p. 83.

(9) J. H. Wise and Milton Volpe, 123rd National A. C. S. meeting, Los Angeles, March, 1953.

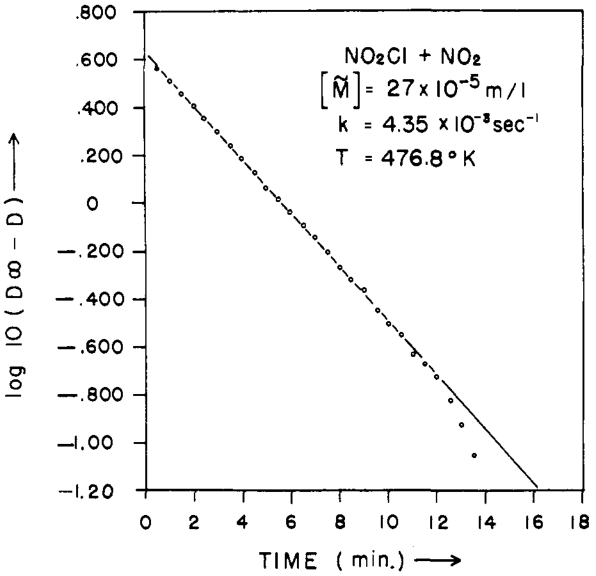

Fig. 1.—Rate plot for five half-lives.

and the first-order rate constant (based on log$_e$) was computed. Also the slope was obtained by the method of least squares, omitting the point at zero time. Although the graphical values and least-squares values agreed very well, all rate constants reported here were based on least squares.

Results

The purity of nitryl chloride was established by chemical analysis and other means as described above. The stoichiometry was confirmed by letting the reaction go to completion. The rate of the reaction is first order for at least five half-lives, as can be seen in Fig. 1, and absence of a positive curvature in this figure implies no inhibition by nitrogen dioxide, that is, there is no evidence for the reverse of reaction (1). For long term runs with no added gas, however, the plot of log [NO_2Cl] against time showed a very slight negative curvature, because the products are more efficient energy transfer agents than the reactant. When the first-order rate constants obtained with the pure reactant were plotted against initial concentration, it was found again[2] that these quantities are directly proportional (Fig. 2), and thus we are in the second-order region of the unimolecular reaction. For constant initial concentrations of reactant (about 9.3 × 10^{-5} mole/liter) runs were made with various

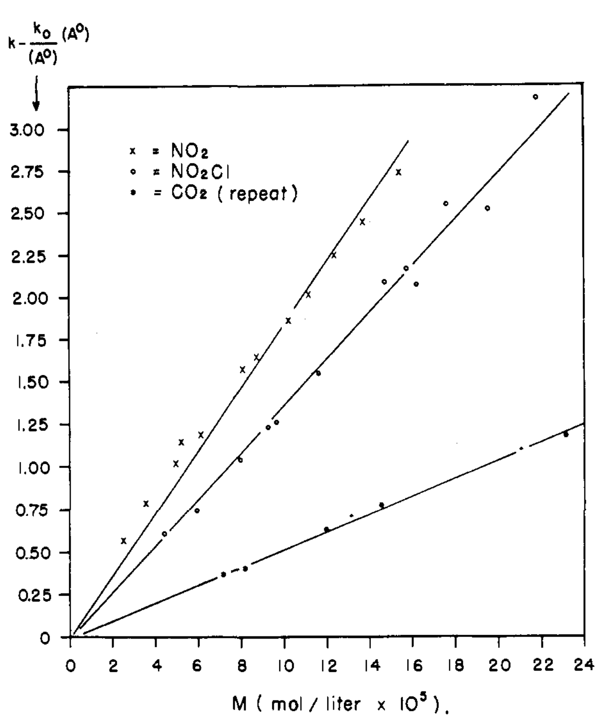

Fig. 2.—Increase in first-order rate constant as a result of the addition of various concentrations of M.

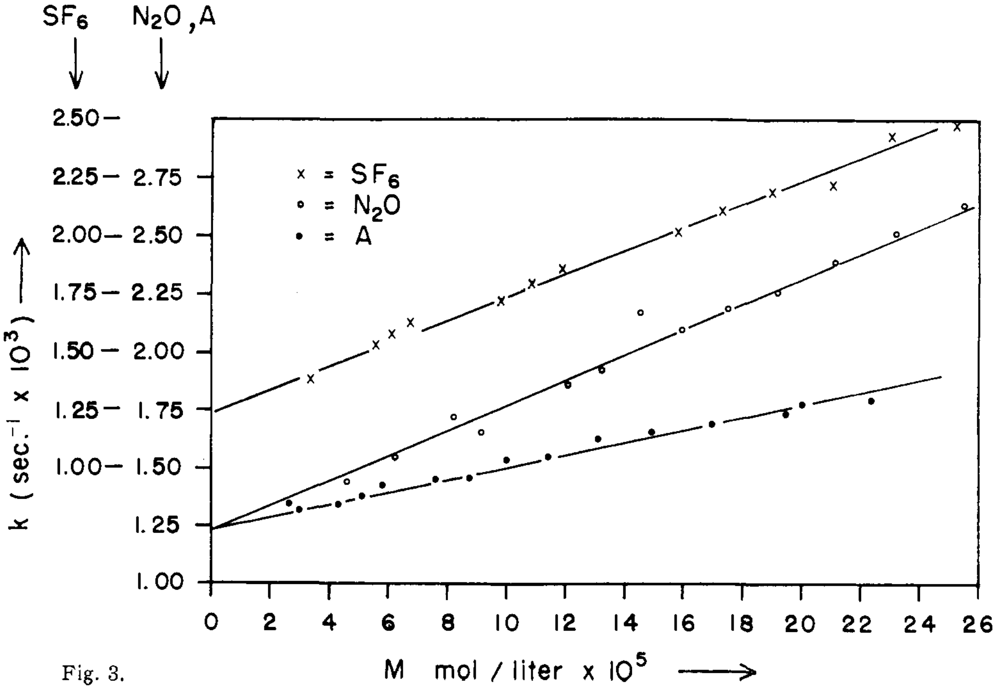

Fig. 3.

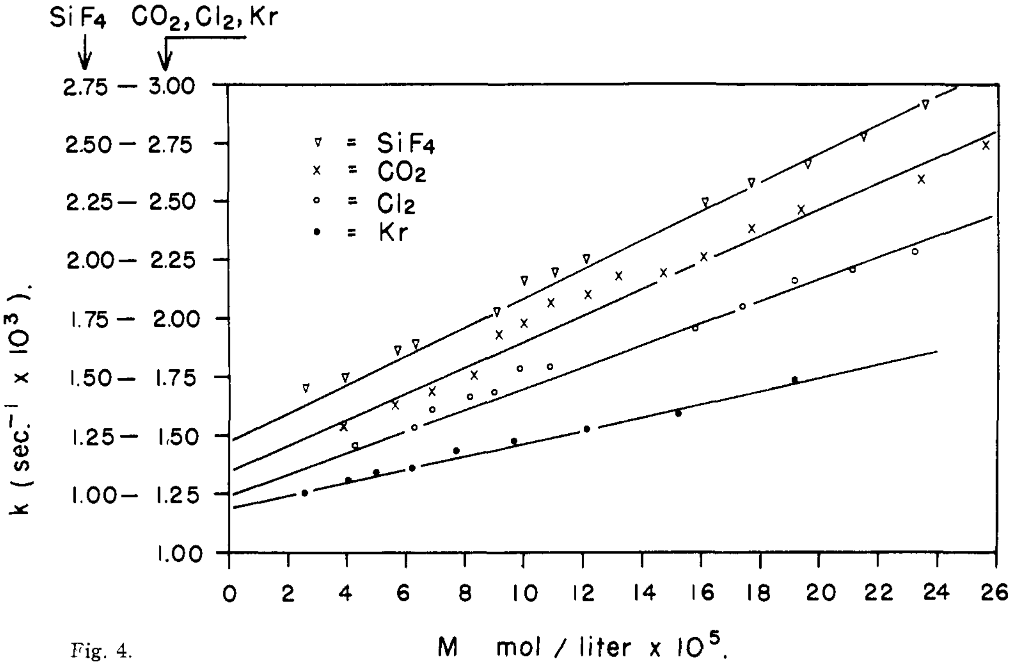

Fig. 4.

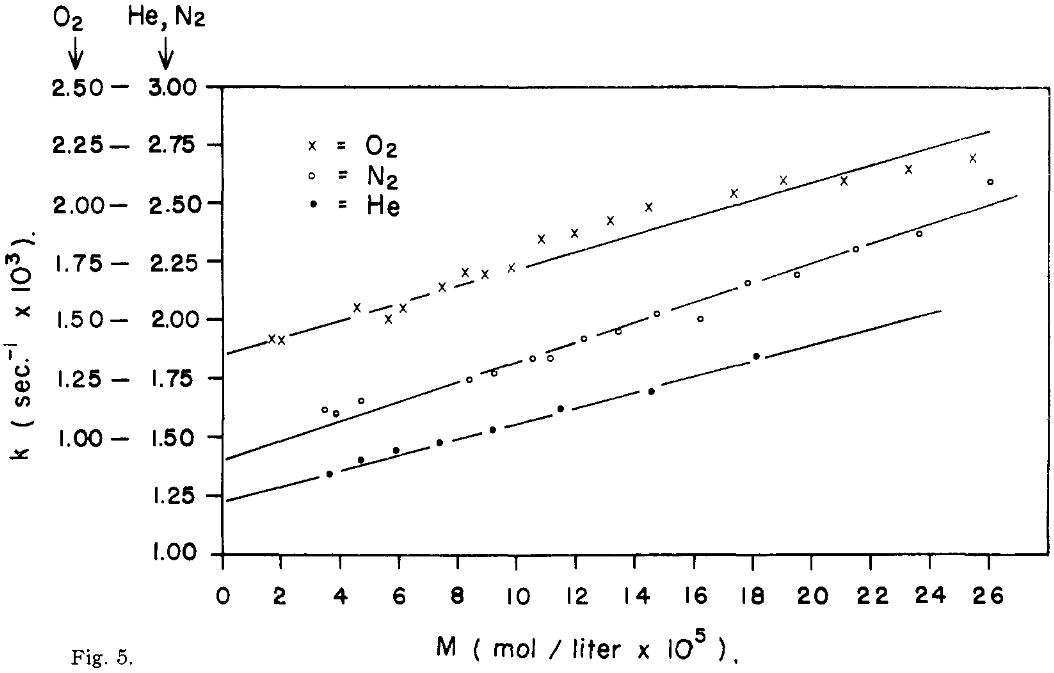

Fig. 5.

amounts of added gases; all the data for 14 different added gases are presented in Figs. 3–6. The lines shown in these figures are based on least-squares and the assumption that the reactant concentration was the same for all runs in a series. Actually there were slight variations, and thus for each series the relative rate constants for activation were found by the method of least squares for the relation

$$k = a_A[A] + a_m[M] \qquad (6)$$

in which both [A] and [M] are treated as variable. Thus for each foreign gas there was found an estimate of a_A and a_m, and the value of $R_m = a_m/a_A$ was obtained from the value of a_A found along with the given a_m. All rate constants obtained in this study and the detailed temperatures and pressures are obtainable as microfilm copies of the thesis.[1] All values of a_A, a_m, R_m and ρ_m are given in Table I. The values of σ in Table I are based on the second virial coefficient and the Lennard-Jones potential.[10]

The purpose of this study was to obtain *precise* data for energy transfer parameters in the second order-region of a unimolecular reaction, and thus an analysis of precision is in order. For each

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(10) The second virial coefficient of nitryl chloride and its temperature dependence were evaluated in this Laboratory by Mr. James Hawes.

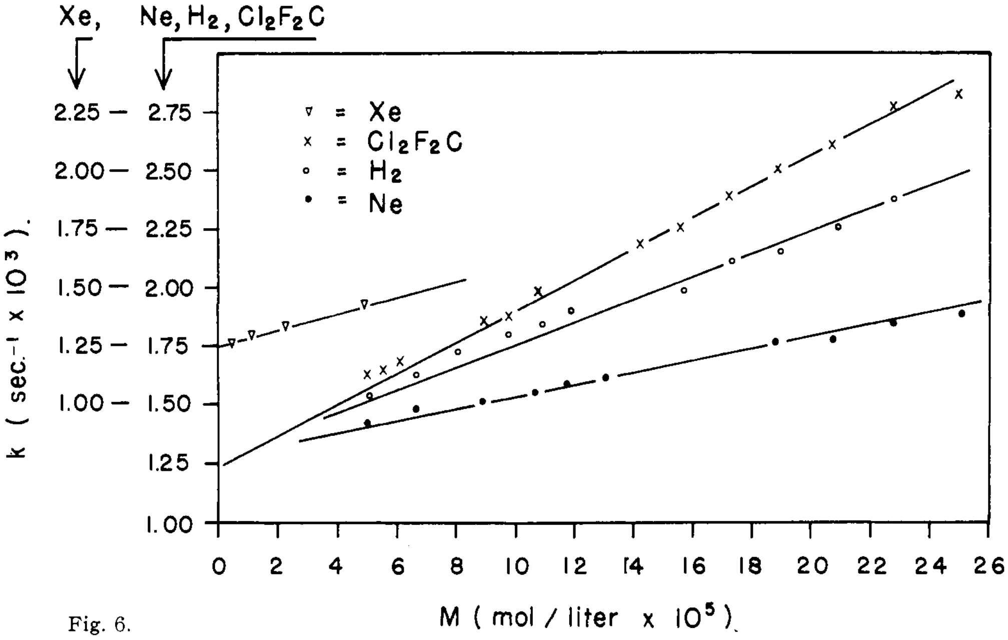

Fig. 6.

Figs. 3–6.—Empirical first order rate constant k for constant initial concentrations of reactant plotted against concentration of M for various foreign gases.

series of runs an estimate is made of the standard error of a_A; these estimates varied from 0.2 to 1.0 in the units of Table I, and they average 0.6. A completely separate estimate of this error is made by analysis of the 18 different values of a_A in Table I; the standard deviation of these numbers is 0.5. The agreement of the standard deviation found by these two methods gives a crude indication that the variation in a_A *could* be due to random errors, and the precision is about 3.5%. The average standard deviation of a_m is about 3%. Thus the probable standard error of R is about 5%, and aside from possible systematic error in the values of σ an error of about 5% is expected for ρ also. The two separate series with carbon dioxide differ by 4%. It appears that despite elaborate precautions to obtain precise data, by the time they are differentiated once to give k and again to give a_A and a_m, the final result is no better than 5%.

Discussion

Mechanism Considerations.—Our previous study[2] confirmed Schumacher and Sprenger's mechanism,[5] eq. 1 and 2, in considerable detail for the case of pure reactant or the reactant plus argon. However, in the present case consideration must be given to possible chemical reactions between chlorine atoms and certain foreign gases, namely, hydrogen, hydrogen chloride and oxygen. For added hydrogen one must consider the following series

$$H_2 + Cl = HCl + H \qquad (7)$$
$$NO_2 + H = NO + OH \qquad (8)$$
$$NO_2 + OH = HNO_3 \qquad (9)$$
$$NO_2Cl + NO = NO_2 + NOCl \qquad (10)$$
$$NO_2Cl + H = NO_2 + HCl \qquad (11)$$

Except for (11) all of these reactions are known to be rather fast. Reactions (7) and (11) together are the same as (2) so far as appearance of nitrogen dioxide is concerned. Reactions (8) and (10) lead to nitrosyl chloride which was looked for but not observed. We have noticed hydrogen chloride and nitryl chloride to react heterogeneously at room temperature in small glass bulbs and in cold traps to produce nitrosyl chloride; thus by means of indirect evidence we conclude (7) did not occur. The rate of reaction (7) is given by[11]

$$k = 10^{10.9}\exp(-5500/RT)\text{l./mole-sec.}$$

and thus the rate of (2) may be expected to be very much faster than this.

Hydrogen chloride as an added gas differed from all others in that some nitrosyl chloride was found in the liquid nitrogen cooled trap after being pumped out of the reaction flask. Our evidence is inconclusive whether the reaction occurred entirely in the small glass leads or partly in the 50-liter reactor. In view of possible chemical complexity for this gas, deductions about its relative efficiency for energy transfer should be regarded as tentative.

Oxygen might add to a chlorine atom to give peroxy—ClO_2, but if followed by $NO_2Cl + ClOO \rightarrow NO_2 + Cl_2 + O_2$, there is no difference in any observable respect between this secondary process and reaction (2).

Relative Efficiencies of Reactants and Products.—The relative efficiency of the products

$$\bar{R} = R_{NO_2} + {}^1/_2R_{Cl_2} \qquad (12)$$

has the numerical value of 1.41, and thus is substantially different from the reactant. The effect of this situation on a plot of log $[NO_2Cl]$ against time is much less than might have been expected; conversely the linearity or not of such a plot is a very insensitive test of whether reactants and products have the same efficiency. This problem

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[11] P. G. Ashmore and J. Chanmugan, *Trans. Faraday Soc.*, **49**, 254 (1953).

TABLE I

THE EXPERIMENTAL RATE CONSTANTS FOR ACTIVATION, RELATIVE RATE CONSTANTS FOR ACTIVATION AND RELATIVE EFFICIENCY FOR ENERGY TRANSFER COLLISION-PER-COLLISION

M. gas	No. of runs	a_A l. mole-sec.	a_m	R_m	Mol. wt.	σ, Å.	ρ_m	k/k_0[a]
NO_2Cl	12	13.7 ± 0.2	....	1.00	81.5	6.7	1.00	1.050
He	10	13.4 ± .7	3.32 ± 0.08	0.247	4.0	2.6	0.15	1.054
Ne	15	13.9 ± .9	2.48 ± .07	.179	20.2	2.8	.22	1.053
A	18	13.4 ± 1.0	2.82 ± .10	.211	39.9	3.4	.30	1.051
Kr	13	13.1 ± .7	2.74 ± .06	.209	83.8	3.6	.36	1.048
Xe	7	13.5 ± .6	3.59 ± .20	.265	131.3	4.0	.46	1.056
H_2	13	14.1 ± .2	4.80 ± .17	.341	2.0	2.9	.15	1.050
N_2	20	14.7 ± .2	4.20 ± .12	.286	28.0	3.7	.34	1.053
O_2	23	14.1 ± .3	3.68 ± .14	.261	32.0	3.5	.34	1.055
Cl_2	17	13.9 ± .2	4.65 ± .12	.335	70.9	4.4	.50	1.048
HCl	9	14.7 ± .7	7.55 ± .40	.513	36.5	(4)	.63	1.048
CO_2	19	14.0 ± .2	5.49 ± .18	.392	44.0	4.1	.50	1.053
CO_2	19	14.0 ± .2	5.23 ± .05	.373	44.0	4.1	.48	1.053
N_2O	18	13.3 ± .2	5.44 ± .14	.409	44.0	4.6	.48	1.050
NO_2	16	14.2 ± .4	17.6 ± .3	1.24	46.0	(5)	1.38	1.038
SiF_4	18	13.4 ± .6	6.12 ± .5	0.456	185.6	6.3	0.51	1.050
SF_6	19	13.7 ± .2	4.92 ± .1	.358	227.6	5.5	.49	1.050
CCl_2F_2	17	13.5 ± .2	6.62 ± .1	.489	202.4	4.9	.71	1.043
Av.		13.8 ± .5						

[a] The error introduced into a_m by virtue of high efficiency of the products relative to the reactant. This error is about the same for all foreign gases as well as for the reactant, and the error introduced in R or ρ is much less than 1%. See succeeding article by Volpe and Johnston, THIS JOURNAL, **78**, 3910 (1956).

is analyzed in detail in the article following this one. This detailed analysis of $\bar{R} \neq 1$ shows that the effect on $R_m = a_m/a_A$ is negligible for the experimental conditions and method of analyzing data which were used here.

Empirical Correlations.—After one accounts for the effect of mass and size on the collision rate, there remains the ratio ρ, the relative efficiency of energy transfer collision-per-collision. The discussion in this section is based on ρ.

In quantitative calculations of the fall-off of the high pressure rate constant with decreasing pressure, all theories of unimolecular reactions, for example, Rice–Ramsperger–Kassel, N. B. Slater, R. A. Marcus, contain the assumption that deactivation occurs on every collision. If this assumption is true for reactant–reactant collisions, then no foreign gas could have a value of ρ greater than one. If this assumption is true for all gases, then the value of ρ is one for all gases. For nitrogen dioxide ρ is about 1.4, and for the other gases it varies from about 0.15 to 0.7. Clearly deactivation does not occur on every collision for all foreign gases, and whether it occurs upon every collision by the reactant is open to grave question. Until this point is cleared up by energy transfer studies, there is no complete quantitative theory of unimolecular reactions.

For the noble gas series ρ is seen to increase steadily from helium through xenon. Inasmuch as atomic mass, number of electrons, size and polarizability all increase together, these data cannot indicate which parameters are important in determining energy transfer efficiency (the same trend is evident in the diatomic non-polar group, hydrogen, nitrogen, oxygen and chlorine).

For spherical molecules of approximately the same mass, xenon, silicon tetrafluoride and sulfur hexafluoride, the values of ρ are, respectively, 0.46, 0.51 and 0.49. Apparently there is little or no correlation of relative efficiency of energy transfer and molecular complexity, that is, the number of atoms or number of oscillators for these examples.

At more or less constant molecular weight and number of atoms, the gases with permanent dipole moments give rather large energy transfer efficiencies, as can be illustrated by the following pairs

O_2	0.34	SiF_4	0.51	CO_2	0.49
HCl	.63	CCl_2F_2	.71	NO_2	1.38

Another empirical relationship which points to the importance of dipole–dipole interaction is the non-linear trend between hydrogen, hydrogen chloride and chlorine, respectively, 0.15, 0.63, 0.50.

A crude but convenient[12] way to test for an empirical relationship between molecular interaction effects and energy transfer effects is to make a plot of relative efficiency ρ against boiling point of the foreign gas, Fig. 7. There is a strong correlation here, especially for the non-polar gases. It appears that the parameters which determine the boiling point are the factors which determine energy transfer efficiency; presumably these factors are intermolecular interaction potentials, and the number of oscillators seems to have little or nothing to do with the effect.

Correlations with Parameters from the Lennard-Jones Potential.—As an approximate model for molecular interactions by the non-polar foreign gases we take the Lennard-Jones expression

$$V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \qquad (13)$$

For interactions between two gases the "empirical combining rules" are used

$$\epsilon_{Am} = (\epsilon_{AA}\epsilon_{mm})^{1/2} \qquad (14)$$

$$\sigma_{Am} = (\sigma_{AA} + \sigma_{mm})^{1/2} \qquad (15)$$

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[12] K. E. Russell and J. Simons, *Proc. Roy. Soc.* (*London*), **217A**, 271 (1953).

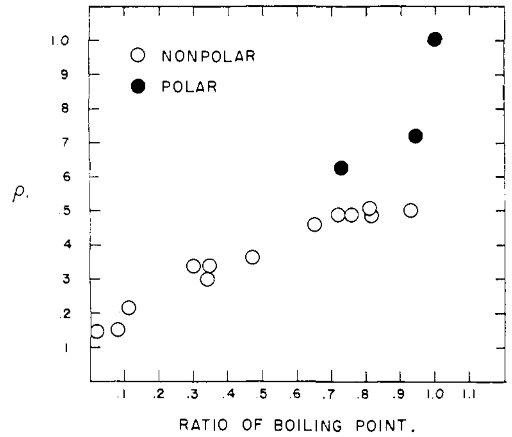

Fig. 7.—Relative efficiency of energy transfer, collision per collision, plotted against ratio of boiling point of M to boiling point of nitryl chloride. All molecules are included except nitrogen dioxide.

The values of ϵ_{mm} and σ_{mm} are obtained from the literature,[13-15] and for nitryl chloride the values (σ = 6.7 ± 0.6 Å.; ϵ/k = 200 ± 45) were found from the second virial coefficient and its temperature variation.[10]

A "soft" collision or one with a small force acting over a large distance would be expected to accelerate the center of mass of the reactant molecule without any considerable "compression of the springs." On the other hand, a hard collision or one with a large force acting quickly against an outer atom of the molecule might be expected to compress the bond to give vibrational excitation (or de-excitation, depending on phases). Admittedly this is a crude and mechanical discussion of activation, but it does suggest plotting ρ against the "force" of the collision, which is readily obtained from the Lennard-Jones potential[13]

$$F = -(\mathrm{d}V/\mathrm{d}r)_{r=\sigma} = 24\epsilon/\sigma \qquad (16)$$

This plot is given in Fig. 8. For the non-polar molecules the plot of ρ against the "force of collision" shows very high correlation, almost a direct proportionality.

It should be emphasized that many parameters associated with molecular interactions go together: mass, number of electrons, size, polarizability, ϵ, $F_{r=\sigma}$, duration of collision, boiling point, etc. These quantities are intimately related, in some cases by cause and effect relations and some are composites of other terms (to Lennard-Jones approximation). Though these data seem to show a strong correlation between ρ and $F_{r=\sigma}$, it must be kept in mind that the correlation may be accidental, some other related factor being the true cause.

Comparison with Other Studies.—Our previous study[2] in the same pressure range gave R = 0.223 for argon; the present work gives R = 0.211. Schumacher and Sprenger[5] studied the relative efficiency of several foreign gases at 140° and between 150 and 500 mm. by the "pressure-for-pressure" method.[5,8] A comparison of results is given in Table II; it is readily seen that the two studies are in total disagreement.

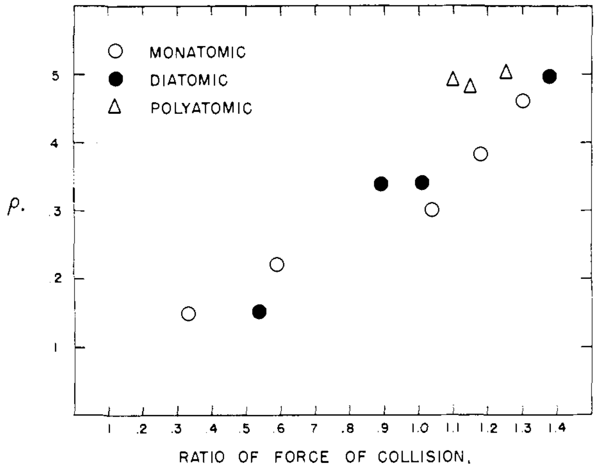

Fig. 8.—Relative efficiency plotted against ratio of the force of A–M collision to A–A collision. Points are plotted only for molecules listed in ref. 13.

TABLE II

COMPARISON OF PRESENT RESULTS WITH THOSE OF SCHUMACHER AND SPRENGER FOR THE QUANTITY R

M. gas	Present work 203° (3–9 mm.)	S and S 140° (150–500 mm.)
NO_2Cl	1.00	1.00
NO_2	1.24	0.54
Cl_2	0.34	.17
O_2	.26	.19
CO_2	.38	.16
H_2	.34	.17

The discrepancies shown in Table II may indicate large unsuspected systematic errors in either our work or in Schumacher and Sprenger's, or on the other hand, it may illustrate a real effect which we anticipated previously[16] and which will be briefly restated for the special case at hand. The rate constant function b_{mi} for deactivation over the states i of the reactant molecule may have the kinetic collision constant b_m factored out to leave an efficiency function

$$b_{mi} = b_m f_{mi}$$

A necessary and sufficient proof[16] may readily be given that if f_{mi} varies strongly over the states i and that if this variation over i is strongly different depending on the identity of the foreign gas M, then relative efficiencies pressure-for-pressure will depend on the reference pressure and on the pressure interval. No matter how complicated a function over i the efficiency function may be, no difference in R will occur if f_{mi} can for all m be factored as $f_m \phi_i$; conversely if any *real* experimental variation is observed, then f_{mi} cannot be so factored (obviously one must be extremely careful not to ascribe some systematic experimental error to this effect). We hope in the future to check Schumacher and

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[13] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954.

[14] J. O. Hirschfelder, F. T. McClure and I. F. Weeks, *J. Chem. Phys.*, **10**, 201 (1942).

[15] S. D. Hamann, W. J. McManamly and J. F. Pearce, *Trans. Faraday Soc.*, **49**, 351 (1953).

[16] H. S. Johnston, Third Technical Report, Section 5, ONR Contract N6 onr 25131, Project NR-051-246 (1953).

Sprenger's work under their conditions of temperature and pressure; meanwhile the interpretation of Table II is ambiguous.

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Effect of Products on Energy Transfer Rates in Unimolecular Reactions

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If the products of a unimolecular reaction have an activating efficiency different from the reactant, the observed first-order rate constant k varies with time throughout the course of an experiment. In the low pressure region where the observed rate is the rate of activation, this effect can be analyzed quantitatively. The ratio $k(t)/k_0$ depends on (1) the method of analyzing data, that is, differential slope, single observation, or method of least squares; (2) the relative efficiency for reactants and products, $\overline{R}$; (3) the amount of added inert gas M relative to initial reactant A_0; and (4) the time of observation relative to the mean time of the reaction. Equations are derived for the effect of all of these parameters and methods, and illustrative graphs are given for special cases.

In the low pressure second-order region of a unimolecular reaction the rate is given by[1,2]

$$\text{Rate} = [\text{A}]\sum_{\text{m}}\sum_{\text{i}} a_{\text{mi}}[\text{M}_{\text{m}}] = [\text{A}]\sum_{\text{m}} a_{\text{m}}[\text{M}_{\text{m}}] \qquad (1)$$

where i denotes quantum states of the reactant which lead to reaction and m denotes identity of the gases present. For the reaction

$$\text{A} \longrightarrow r\text{B} + s\text{C} \qquad (2)$$

in the presence of one inert foreign gas M the rate constant expression is

$$k = a_1[\text{A}] + a_2[\text{B}] + a_3[\text{C}] + a_4[\text{M}] \qquad (3)$$

By virtue of stoichiometry this expression reduces to

$$k = a_1[\text{A}_0] + a_4[\text{M}] - (a_1 - ra_2 - sa_3)([\text{A}_0] - [\text{A}]) \qquad (4)$$

where subscript zero refers to initial conditions. By definition[1] the relative efficiency is $R_{\text{m}} = a_{\text{m}}/a_1$. The "relative efficiency of products" is defined as

$$\overline{R} = ra_2/a_1 + sa_3/a_1 \qquad (5)$$

The initial equivalent concentration[1] is

$$[\text{M}_0] = [\text{A}_0] + \text{R}_4[\text{M}] \qquad (6)$$

Therefore the rate constant expression is

$$k = a_1[\text{M}_0] - a_1(1 - \overline{R})([\text{A}_0] - [\text{A}]) \qquad (7)$$

The differential rate constant at the initial time is

$$k_0 = a_1[\text{A}_0] + a_4[\text{M}] = a_1[\text{M}_0] \qquad (8)$$

The rate constant will have this value throughout the course of the reaction if and only if the products have the same efficiency as the reactants, or $\bar{R} = 1$. If $\bar{R}$ is not unity, the reaction will not be strictly first order throughout a run; the rate expression is

$$-(1/[\text{A}])\,\text{d}[\text{A}]/\text{d}t = k_0 - a_1(1 - \overline{R})([\text{A}_0] - [\text{A}]) \qquad (9)$$

which is of the form

$$-\text{d}[\text{A}]/\text{d}t = \alpha[\text{A}] + \beta[\text{A}]^2 \qquad (10)$$

where $\alpha = k_0 - \beta[\text{A}_0]$ and $\beta = a_1(1 - R)$. Equation 10 may be integrated to give

$$y = \log\frac{[\text{A}_0]}{[\text{A}]} = \alpha t + \log\left\{1 + \beta\frac{[\text{A}_0]}{\alpha}(1 - e^{-\text{at}})\right\} \qquad (11)$$

For $0.5 < \bar{R} < 2$, or for wider limits in the presence of a foreign gas, eq. 11 may be expanded to any desired degree of approximation.

$$\frac{y}{k_0t} = 1 - \frac{k_0t}{2}(1 - \overline{R})\frac{[\text{A}_0]}{[\text{M}]} + \frac{(k_0t)^2}{6}(1 \quad \overline{R})\frac{[\text{A}_0]}{[\text{M}]}\left\{1 - (1 - \overline{R})\frac{[\text{A}_0]}{[\text{M}]}\right\} - \cdots \qquad (12)$$

If one has a series of observations y_{j} at a series of equally spaced times t_{j} and if these observations are forced by the method of least squares to fit the first-order relation

$$y = kt + l \qquad (13)$$

the value of the slope is given by solving for k from

$$\begin{aligned} \Sigma y_{\text{j}} &= k\Sigma t_{\text{j}} + nl \\ \Sigma y_{\text{j}}\, t_{\text{j}} &= k\Sigma t_{\text{j}}^2 + l\Sigma t_{\text{j}} \end{aligned} \qquad (14)$$

where n is the number of observations. By substitution of $t = x + \bar{t}$ where $\bar{t}$ is the middle time, one obtains

$$k = \Sigma x_{\text{j}}y_{\text{j}}/\Sigma x_{\text{j}}^2 \qquad (15)$$

By substitution of (12) into (15) and use of the fact that summation of odd powers of x is zero by symmetry, one finds, to an excellent approximation, that eq. 12 is recovered with t replaced by $t/2$ or $\bar{t}$.

For experimental data of extremely high precision one may use the differential method of finding rate constants, and the effect of products is given directly by eq. 9. For runs in which a single observation is made of [A] and t in addition to $[\text{A}_0]$, the error introduced by efficiency of products as measured by the ratio k/k_0 is given by eq. 12. For runs in which numerous equally spaced observations are made from 0 to t and for which a first-order constant is obtained by least squares, the ratio k/k_0 is also given by eq. 12 with t replaced by $\bar{t}$ or $t/2$. Further discussion is restricted to the case using least squares.

The ratio of the apparent slope k to the initial slope k_0 is a dimensionless number characterizing the error introduced by unequal efficiency of react-

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[1] Terminology used in this article is that of H. S. Johnston, THIS JOURNAL, **75**, 1567 (1953); *J. Chem. Phys.*, **20**, 1103 (1952).

[2] M. Volpe and H. S. Johnston, THIS JOURNAL, **78**, 3903 (1956).