is the evaluation of $\rho(Y)$. However, the fused ring A may be considered as a constant *ortho* substituent, and hence probably does not affect $\rho(Y)$.[2] An additional term X[13] would have to be introduced into the second line of equation 3. Then application of equation 3 also permits evaluation of substituent constants for the 6- and 7-positions of naphthalene derivatives undergoing reaction at a side chain in the 1-position. Such substituent constants, however, would have to be used together with the X-terms, which must be evaluated separately for each reaction series. Similar arguments may also apply to quinoline and isoquinoline derivatives having reacting side chains. Unfortunately, sufficient experimental data to use the relations derived do not appear to be available at present.

A few comments concerning the calculations are necessary. Only reaction series for which data were available for more than 4 compounds were used. All data were fitted to equation 2 by the use of standard methods of multiple correlation.[8] The difference of a given value of ρ from zero was tested by use of Student's $t = \rho/s_\rho$.[14] Analysis of variance[15] was used to test whether or not equation 2 represented a given set of data *significantly*[9] better than the use of equation 1 alone.

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(13) See equation 7 of reference 2b.

(14) Reference 8, p. 62.

(15) Reference 8, Chapters X and XI.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, CALIFORNIA]

Thermal Decomposition of Nitryl Chloride. I. Second-order Unimolecular Rate Study

BY HERMAN F. CORDES[1] AND HAROLD S. JOHNSTON

RECEIVED MARCH 20, 1954

The thermal decomposition of nitryl chloride has been reinvestigated at low pressures in a 50-liter Pyrex flask from 180 to 250°. The mechanism of Schumacher and Sprenger has been confirmed, and although present conditions never coincide with those of the previous study, the results appear to be in essential agreement. The observed rate is twice that of the elementary unimolecular decomposition $NO_2Cl = NO_2 + Cl$. The results show quite clearly that the reaction is first order in reactant throughout a single run, and the first-order rate constants are themselves first order in initial concentration. Thus these results provide an illustration of the second-order region of a unimolecular reaction. The effect of argon was studied, and the results are that argon does not deactivate excited nitryl chloride upon every collision. The number of normal modes contributing to the reaction coördinate was computed by the Kassel-Slater method and found to be six, the number of normal modes of the molecule itself.

Introduction

Schumacher and Sprenger reported the thermal decomposition of nitryl chloride

$$NO_2Cl = NO_2 + {}^1/_2Cl_2 \tag{1}$$

to be a first-order homogeneous gas phase reaction.[2] The data obtained by these workers were in the mid-range between the high and low concentration regions. The mechanism for this reaction was suggested as being

$$NO_2Cl \longrightarrow NO_2 + Cl \quad k_1 \tag{2}$$

$$NO_2Cl + Cl \longrightarrow NO_2 + Cl_2 \quad k_2 \tag{3}$$

From this mechanism and the assumption of a steady state for chlorine atom concentration, the empirical first-order rate constant can be identified with $2k_1$. It was felt that this reaction offered a good chance to obtain a clear-cut example of the region of second-order kinetics for a unimolecular reaction.[3]

Experimental

Materials.—Nitryl chloride was prepared by the method previously described.[4] Nitrogen dioxide was obtained from Matheson Co. and purified to oxidize the nitric oxide and to remove any nitric acid if present. Argon from the Matheson Co. was passed through a liquid nitrogen trap.

Apparatus.—The reaction vessel was a 50-liter Pyrex flask with quartz windows attached through a short graded seal. These windows were inset 7 cm. into the flask. The flask was placed in a double-walled steel furnace; the space between the walls was filled with 14 cm. of insulation, Monsanto Santo-Cel A. The top of the furnace was covered with 3 cm. of molded magnesia insulation and 3 cm. of fiber glass insulation. The flask rested on a sand-bath inside the furnace. Air inside the furnace was stirred strongly by a large blower which connected through the furnace wall to an external electric motor. A 20-ohm Chromel resistance heating wire was wound uniformly around the walls on the inside of the furnace, and by means of a stabilized power source (Superior Electric Co., Stabiline Electromechanical Voltage Regulator) and a variable transformer, the furnace was heated to within about 5° of the desired temperature. The final temperature control was obtained with two cone heaters mounted close to the blower in the bottom of the furnace and connected through a mercury switch to a thermometer control switch. Temperature, read by a mercury thermometer calibrated against a Pt-Rh thermocouple, was constant in time to 0.1° and was uniform over the bulb to 0.5°.

Reactant gas was stored in a 22-liter storage bulb blackened to prevent photochemical decomposition of nitryl chloride. Pipet bulbs, 0.01 the volume of the reaction flask, were filled with nitryl chloride, and the pressure was read on a glass bourdon gage used as a null instrument. The sensitivity of this gage was about 0.5 mm. and pressures were usually read in the range of 100 to 600 mm. Stopcocks were hollow specially ground high-vacuum type greased with polychloro-trifluoroethylene stopcock grease. This grease is not attacked by nitryl chloride, but it showed a vapor pressure of about 0.05 mm. on a thermocouple pressure gage.

Calibration.—The course of the reaction was recorded by following colorimetrically the nitrogen dioxide produced. The light source was a stabilized A-H4 mercury arc filtered

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(1) The material for this article was abstracted from a dissertation submitted in partial fulfillment of the requirements for the Ph.D. degree at Stanford University, 1954.

(2) H. J. Schumacher and G. Sprenger, *Z. Elektrochem.*, **35**, 653 (1929); *Naturwissenschaften*, **17**, 997 (1929); *Z. physik. Chem.*, **B12**, 115 (1931).

(3) Discussion with S. W. Benson at symposium on very fast reactions, Atlantic City, N. J., September, 1952; *J. Phys. Chem.*, **57**, 424 (1953).

(4) E. C. Freiling, H. S. Johnston and R. A. Ogg, Jr., *J. Chem. Phys.*, **20**, 327 (1952).

by a heat filter and Corning filters 5113 and 3389 to remove all lines except that at 436 mμ. The light was focused through the flask onto RCA 1-P28 photomultiplier tube mounted outside the furnace. The output of the phototube was sent to a high precision electronic voltmeter and readings were taken visually. Known concentrations of nitrogen dioxide inside the furnace were prepared by emptying the pipets, filled to a known pressure, into the reaction flask. The Beer's law constant as obtained in this calibration was corrected for the additional absorption due to chlorine which would be present in an actual decomposition. This correction amounted to 0.5%.

In making a run, the dark current of the phototube was corrected in the voltmeter, and the intensity of the light passing through the evacuated flask recorded as I_0. A previously measured pressure of nitryl chloride was then introduced into the reaction flask. In order to assure temperature and pressure equilibrium, the reaction flask remained connected to the pipet system for 15 seconds after the introduction of the nitryl chloride. After this delay, the flask was isolated from the pipet system and timed readings of the light intensity were taken.

The concentration of nitrogen dioxide at each time was calculated from the corrected Beer's law constant. The nitryl chloride concentration at any time was then calculated from the corresponding nitrogen dioxide concentration and the initial nitryl chloride concentration.

Results

Stoichiometry.—A few of the runs with pure nitryl chloride were allowed to proceed to completion (10 half-lives or more). The final nitrogen dioxide, determined optically, was equal within experimental error, ±2%, to the initial nitryl chloride concentration. The final pressure was three-halves of the initial nitryl chloride pressure with an error of ±2%. These results confirm the stoichiometry suggested by Schumacher and Sprenger,[2] eq. 1.

Order with Respect to Reactant During One Run.—Nitrogen dioxide concentration at each time during a run was calculated from voltmeter readings and the calibration curve. The value of nitrogen dioxide concentration was subtracted from the initial nitryl chloride concentration to give nitryl chloride concentration at each time. The integrated rate expression for a first-order reaction gives a linear relation between *log reactant vs. time.* A sample test of this relation is shown in Fig. 1 and these results show that the reaction is first order in nitryl chloride during a single run. The slope of the line multiplied by −2.303 gives the empirical first-order rate constant. Figure 1, like most runs made in this study, is for only a small degree of reaction (about 20% in this case), and thus the rates measured were more or less initial rates. In some cases the reaction was followed almost to two half-lives, and the first-order relation was followed throughout.

Order with Respect to Total Initial Pressure.—A series of runs at different initial concentrations of nitryl chloride was made at 180, 203, 227 and 248°.

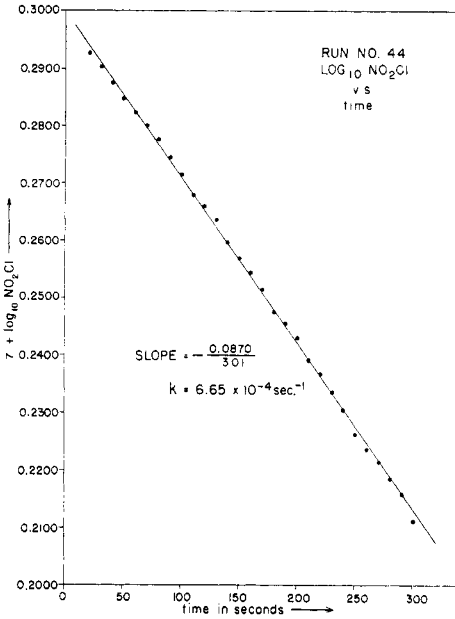


Fig. 1.—Test of integrated rate equation for first-order reaction during a single run.

For each run the empirical first-order rate constant was found as with Fig. 1, and the linear relation during a given run was seen in all cases. Plots, at each temperature, of the empirical first-order rate constant against total initial concentration are shown in Figs. 2–5. In all cases the first-order rate constant is directly proportional to the initial concentration of reactant. Thus the slopes in Figs. 2–5 represent second-order rate constants. The points in these figures were fitted by the method of least squares to the relation

$$k = A + B[\mathrm{M}] \qquad (4)$$

$$k/[\mathrm{M}] = C + D[\mathrm{M}] \qquad (5)$$

If the first-order constants are indeed directly proportional to initial reactant concentration [M], then *A* and *D* should be zero within experimental error, and *B* and *C* should be the same. The values listed in Table I indicate that within experimental error these conditions are met, at least at the higher temperatures.

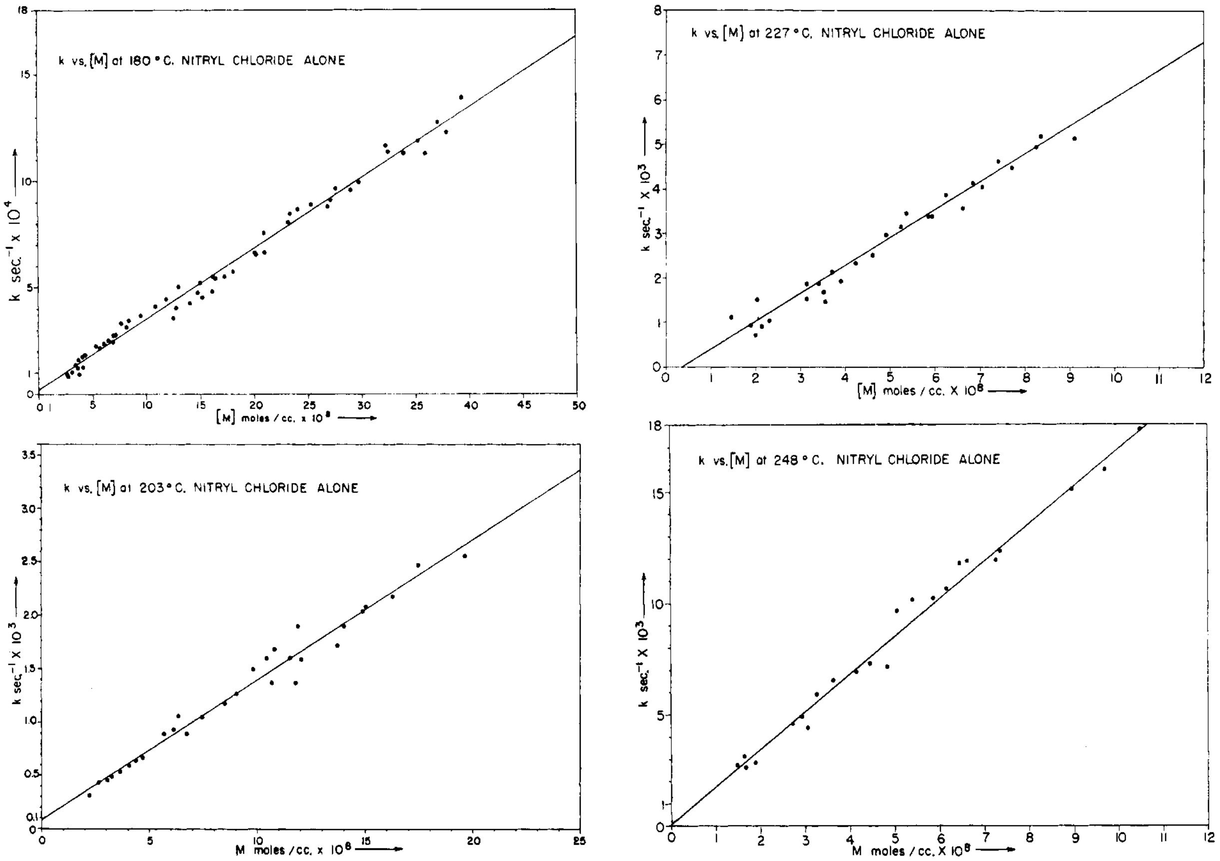
A series of runs employing argon as foreign gas was made at 180°. The order during a single run was still first order in nitryl chloride. A plot of empirical first-order rate constants against total initial concentration is shown in Fig. 6, and it will be noticed that much higher pressures were used in this series than for runs with pure reactant. From Fig. 6 it is seen that at the lower concentrations,

TABLE I

LEAST SQUARE FIT OF THE PARAMETERS, AND THEIR 95% CONFIDENCE INTERVALS, IN EQUATIONS 4 AND 5

Temp., °C.	*A*, sec.$^{-1}$ × 10^5	*B*, (moles/cc.)$^{-1}$ sec.$^{-1}$ × 10^{-3}	*C* (moles/cc.)$^{-1}$ sec.$^{-1}$ × 10^{-3}	*D*, (moles/cc.)$^{-2}$ sec.$^{-1}$ × 10^{-9}
180	2.1 ± 1.9	3.31 ± 0.10	3.69 ± 0.20	−1.1 + 1.0
203	9.4 ± 8.6	13.0 ± 0.80	15.1 ± 0.80	−9.75 ± 0.80
227	−24 ± 22	62.3 ± 4.2	51.8 ± 8.8	96 ± 147
248	13 ± 50	168 ± 10	174 ± 12	−400 ± 214
180	7.9 ± 8.6[a]	0.851 ± 0.14[a]	1.116 ± 0.094[a]	−0.18 ± 0.14[a]

[a] Runs with added argon. Mole fraction NO_2Cl = 0.103. Points used only below $k = 10^{-3}$ sec.$^{-1}$.



Figs. 2–5.—Test for second-order rate. The empirical first-order rate constant is plotted against initial concentration of reactant.

the empirical rate constant is proportional to total initial concentration, but at higher concentrations the rate constants fall below this proportionality curve. Below 0.001 sec.$^{-1}$ for k, the empirical first-order rate constants and total initial concentrations were fitted to eq. 5, Table I. These runs with argon show too much curvature to be fitted accurately to the first of these equations, but the second plot appears to give a good fit.

Nitrogen dioxide is one of the products of reaction, and it was desirable to see if it affected the rate in any strong manner. At 248° seven runs were made over which the ratio of initial nitrogen dioxide to initial nitryl chloride varied from 0.7 to 2.1. During a single run the reaction was first order in nitryl chloride. The first-order rate constant increased with nitrogen dioxide in the same manner ($\pm 20\%$) as with nitryl chloride. Thus it appears that nitrogen dioxide has the same qualitative effect as argon on this reaction at very low pressures, but within an unusually large experimental error its effect as a foreign gas is almost equal to that of nitryl chloride.

Energy of Activation.—The second-order rate constants given by the slope B in eq. 4 and Table I were fit by the method of least squares to the Arrhenius equation, $k = Ae^{-E/RT}$, to give $A = (5.8 \pm 0.4) \times 10^{16}$ cc. mole^{-1} sec.$^{-1}$ and $E = 27.5 \pm 0.1$ kcal. This plot is shown in Fig. 7.

It is difficult to compare the present work with that of Schumacher and Sprenger,[2] because both the pressure and temperature regions differ in the two cases. The very lowest pressure points of Schumacher and Sprenger appear to be partially heterogeneous, and these were excluded; but the remaining points were plotted as $k/[\mathrm{M}]$ *vs.* $[\mathrm{M}]$ and extrapolated to zero $[\mathrm{M}]$. In this way a rough estimate can be made of their second-order rate constants, and these are included on Fig. 7. It can be seen that the earlier work is in essential agreement with this study.

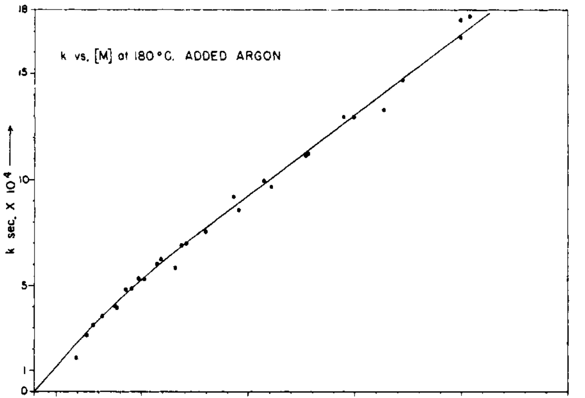


Fig. 6.—Dependence of empirical first-order rate constant on concentration of argon.

Mechanism.—Schumacher and Sprenger proposed 2 and 3 as the mechanism for this reaction.

This mechanism will be accepted as a trial hypothesis, and based on this hypothesis one makes a quantitative estimate of many alternative mechanism steps. The self-consistency and numerical reasonableness of the final results will be used to judge the assumed mechanism. If the mechanism is (2) and (3), then the observed energy of activation, 27.5 kcal., is the low-pressure limit of the unimolecular dissociation (2), and as shown later this leads to the value of 29.5 as the critical energy of (2). The critical energy for the dissociation of chlorine is 57.2 kcal.[5] With these two values, the following heats of reaction at 0°K. may be computed

$$NO_2Cl = NO_2 + Cl - 29.5 \text{ kcal.} \tag{6}$$

$$Cl_2 = 2Cl - 57.2 \text{ kcal.} \tag{7}$$

$$NO_2Cl = NO_2 + {}^1/_2Cl_2 - 0.9 \text{ kcal.} \tag{8}$$

$$NO_2Cl + Cl = NO_2 + Cl_2 + 27.7 \text{ kcal.} \tag{9}$$

By means of the rigid-rotator harmonic-oscillator approximation and the energy terms 6–9, the corresponding equilibrium constants[6] were computed at 500°K.

$$K_6 = [NO_2][Cl]/[NO_2Cl] = 9.6 \times 10^{-12} \text{ mole cc.}^{-1} \tag{10}$$

$$K_7 = [Cl]^2/[Cl_2] = 5.3 \times 10^{-25} \text{ mole cc.}^{-1} \tag{11}$$

$$K_8 = [NO_2][Cl_2]^{1/2}/[NO_2Cl] = 13 \text{ mole}^{1/2} \text{ cc.}^{-1/2} \tag{12}$$

$$K_9 = [NO_2][Cl_2]/[NO_2Cl][Cl] = 1.8 \times 10^{13} \tag{13}$$

Now consider not just the two-step mechanism 2 and 3 but rather several reasonable variations and extensions of it.

$$NO_2Cl \xrightarrow{k_{uni}} NO_2 + Cl \tag{14}$$

$$NO_2 + Cl \xrightarrow{b_{ba}} NO_2Cl \tag{15}$$

$$NO_2Cl + Cl \xrightarrow{e} NO_2 + Cl_2 \tag{16}$$

$$NO_2 + Cl_2 \xrightarrow{f} NO_2Cl + Cl \tag{17}$$

$$2Cl + M \xrightarrow{g} Cl_2 + M \tag{18}$$

$$M + Cl_2 \xrightarrow{h} 2Cl + M \tag{19}$$

A detailed consideration of the unimolecular reaction 14 and the bimolecular association 15 would give

$$k_{uni} = \sum_i \frac{a_i c_i[M]}{b_i[M] + c_i} \tag{20}$$

$$k_{ba} = \sum_i \frac{d_i b_i[M]}{b_i[M] + c_i} \tag{21}$$

and at very low pressures these reduce to $k_{uni} = a[M]$ and $k_{ba} = db[M]/c$.

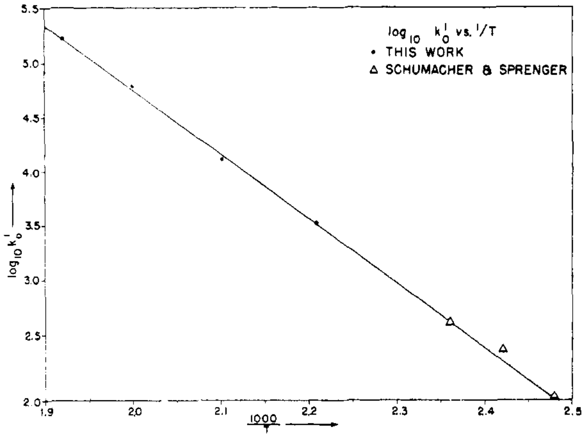


Fig. 7.—Temperature dependence of second-order rate constant and a comparison with previous work (the line is based only on the results reported here).

With these relations one is able to evaluate the relative importance of all the steps (14)–(19). Step h may be dropped at once from energy considerations. The observed rate is twice that for (14), and thus with K_6 one has the numerical value for (15). The value of g is known,[7] 3×10^{14} cc.^{2} mole^{-2} sec.$^{-1}$; a limit can be set on [Cl], namely, the steady-state value for (14) and (18); and one concludes that rate (15) is many more than 10 orders of magnitude faster than (18). Nitrogen dioxide does not inhibit the reaction during the course of one run nor when added initially, and this implies that both (15) and (17) are negligibly slow compared to (14) and (16)—a full algebraic treatment of the complex mechanism leads to the same conclusion, that is, the degree of advancement is independent of [NO_2] only if (15) and (17) are negligible in rate in this system. Since the numerical value of (15) is known, the statement that rate (16) is very fast compared to (15) implies that e is very much greater than 10^{10} cc. mole^{-1} sec.$^{-1}$, not an impossible requirement for an atomic reaction of this type. Since e cannot exceed the collision rate constant 10^{14} cc. mole^{-1} sec.$^{-1}$, it is bounded between 10^{11} and 10^{14}. Using these values and K_9, one concludes that f is between 10^{-2} and 10 cc. mole^{-1} sec.$^{-1}$, and this is consistent with the previous conclusion that rate (17) is negligibly slow compared to (14) and (16). Thus if one takes the general mechanism (14)–(19), one is forced back to the mechanism of Schumacher and Sprenger.

The value of K_8 shows the equilibrium to lie far on the side of the products. If the initial concentration of nitryl chloride was 10^{-7} mole cc.$^{-1}$, its value at equilibrium would be 1.7×10^{-12} mole cc.$^{-1}$. Even at one atm. initial pressure of nitryl chloride, equilibrium at 500°K. would leave only 0.02% of nitryl chloride. The heat of reaction is very nearly zero, and even assuming the maximum probable value, one finds the thermal gradients[8] to be negligible even in the 50-l. flask.

Discussion

Recently Benson[3] expressed doubt as to the existence of an experimentally demonstrated example of second-order kinetics for a unimolecular reaction. The present study was carried out in great detail

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[5] G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950.

[6] Neither the structure nor spectrum of nitryl chloride is known, and so these calculations are based on an assumed model. Nitryl chloride is assumed to be planar, and the chlorine and oxygen atoms are spaced at 120° angles around the central nitrogen atom. The N–O and N–Cl bond distances are assumed to be the same as in nitrosyl chloride (D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944), and the six vibration frequencies are taken to be the same as the frequencies of nitrogen dioxide plus those for nitrosyl chloride. The electronic degeneracy is 2 for nitrogen dioxide, 4 for chlorine atom, and 1 for nitryl chloride and chlorine.

[7] H. J. Schumacher and G. Steiger, *Z. physik. Chem.*, **B13**, 169 (1931); G. Porter, *Proc. Roy. Soc.* (*London*), **A200**, 284 (1950).

[8] S. W. Benson, *J. Chem. Phys.*, **22**, 46 (1954).

in an effort to demonstrate the properties of the second-order region of a unimolecular reaction. Of course, it is only at zero pressure that the order becomes exactly two, even for a single term in the Lindemann summation, eq. 20. At all finite pressures the order is, in principle, somewhat less than precisely two. The experimentally realizable case is that of the first-order rate constant being directly proportional to total concentration (within experimental scatter) and this condition is illustrated in Figs. 2–6. Another demonstration of the same thing is that a plot of $k/[M]$ against $[M]$ should approach zero $[M]$ over a range of $[M]$ with almost no slope; this condition is illustrated by the numbers in Table I. The runs with pure reactants show almost no slope, and the runs with large amounts of argon show that the "fall-off" of the second order rate constant with increasing pressure sets in quite slowly.

Test of Theory of Deactivation upon Every Collision.—It has been pointed out for nitrogen pentoxide that deactivation of an excited reactant molecule does not occur upon every collision by a noble gas molecule,[9] and no possible re-adjustment of collision diameters in the kinetic collision formula could change this conclusion. In the present study it was found that nitrogen dioxide and nitryl chloride are almost equally effective in deactivating nitryl chloride, but for all anyone knows their absolute deactivating efficiency could be 1 or as low as 10^{-3}. In the present study the ratio of second-order rate constant for deactivation of nitryl chloride to argon is 4.48. If this ratio is multiplied by the ratio reduced mass of NO_2Cl–NO_2Cl to NO_2Cl-A the value is 5.53 ± 0.21. But according to the theory of deactivation by every collision this ratio is interpreted as

$$\left(\frac{\sigma_1 + \sigma_1}{\sigma_1 + \sigma_2}\right)^2 \qquad (22)$$

where σ_1 is kinetic collision diameter for nitryl chloride and σ_2 is that for argon. The maximum possible value of this ratio is 4, that is, upon the assumption that $\sigma_2/\sigma_1 = 0$. The observed value is greater than 4. If the errors are all random and the standard deviation is that for the error curve, then the chance that the ratio of rate constants corrected for reduced mass lie between zero and 4 is 10^{-4}. This datum is another example[9] of the conclusion that deactivation of excited reactant molecules does not occur upon every collision by a noble gas molecule.

In the book "Chemische Gasreactionen," Schumacher[10] reports the relative efficiency of several foreign gases, based on the ratio of pressure necessary to produce a given increase in the rate constant at a region far above the second-order limit. From the form of 20, it is not at all obvious that such a "relative efficiency" is the same as the ratio of activational rate constants which is obtained at the low pressure limit. In this table the value for nitrogen dioxide is reported as 0.54 and chlorine is 0.17. The work reported here on nitrogen dioxide was not designed to give an accurate value of relative efficiency but merely to look for a large chemical effect if it existed. Further work will be needed to resolve this slight conflict. Aside from this point, the values of relative efficiency of the various foreign gases also show very strongly the fact that deactivation does not occur on every collision by the foreign gases, and the present confirmation of Schumacher's mechanism should re-establish these results. Furthermore, the same conclusion (deactivation does not occur on every collision by foreign gases whether or not it does for every collision by the reactant gas) can be reached from Table I of relative efficiencies for the various gases added to cyclopropane.[11]

Number of Oscillators in Kassel and Slater Theories.—The critical energy E_0 and the effective number of oscillators s of the classical form of the Rice–Ramsperger–Kassel theory was determined numerically in the manner used previously,[12] except that half integral values of s were not excluded (it will be recalled that this evaluation assumes that deactivation occurs upon every collision by another reactant molecule).

Using 10^{14} cc. mole^{-1} sec.$^{-1}$ for the kinetic collision constant, the values for 3, 3.5 and 4 oscillators are listed in Table II. The best fit seems to be E_c = 29.5 kcal. (in essential agreement with Schumacher[10]) and s = 3.5. N. B. Slater[13] has shown that classical RRK rate becomes identical with his form (apart from a numerical factor which for small molecules is of the order of unity) provided that the oscillators s are related to the number of non-degenerate normal modes n by

$$s = (n + 1)/2 \qquad (23)$$

With this relation one finds $n = 6$ which happens to be equal to the number of normal modes in the molecule.

TABLE II

ESTIMATION OF NUMBER OF OSCILLATORS IN CLASSICAL RRK THEORY

$X_{obs} = 6.5 \times 10^3$ °K.$^{1/2}$

Temp., °K.	s	E_c	$X^a_{calcd.}$ (°K.)$^{1/2}$ × 10^{-3}
453	3	28.8	2.6
	3.5	29.3	5.7
	4	29.7	11.3
476	3	28.9	2.4
	3.5	29.4	5.2
	4	29.9	11.0
500	3	29.0	2.3
	3.5	29.5	4.7
	4	30.0	9.3
521	3	29.1	2.1
	3.5	29.6	4.5
	4	30.1	8.4

[a] $X_{calcd.} = T^{1/2}e^{-(s-3/2)} \sum_{r=0}^{r=s-1} 1/r!(E_c/RT)^r$. $X_{obs} = AT^{1/2}/2b$ where A is pre-exponential factor of empirical rate constant and b is kinetic collision constant with collision diameter of 3.2 Å.

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(9) D. J. Wilson and H. S. Johnston, THIS JOURNAL, **75**, 5763 (1953).

(10) H. J. Schumacher, "Chemische Gasreactionen," Steinkopf, Dresden, 1938, pp. 127–130.

(11) H. O. Pritchard, R. G. Sowden and A. F. Trotman-Dickenson, *Proc. Roy. Soc.* (*London*), **A217**, 563 (1953).

(12) H. S. Johnston and R. L. Perrine, THIS JOURNAL, **73**, 4782 (1951).

(13) N. B. Slater, *Phil. Trans. Roy. Soc.* (*London*), **A246**, 57 (1953).

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STANFORD, CALIFORNIA

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

An Examination of Tin(IV) Solutions in Sulfuric Acid[1]

BY C. H. BRUBAKER, JR.

RECEIVED MARCH 22, 1954

Although tin(IV) is relatively insoluble in sulfuric acid solutions, spectrophotometric and electromigration studies in dilute solutions (*ca.* $10^{-3} f$ Sn(IV)) have been carried out. Examination of the apparent extinction coefficients, at 240 mμ, as a function of sulfuric acid concentration and a similar examination in perchloric acid (which is assumed to be non-complexing) indicate that the following reactions take place: (1) $Sn^{+4} + 2SO_4^{=} \leftrightarrows Sn(SO_4)_2$, K_1; (2) $Sn(SO_4)_2 + H_2SO_4 = H_2Sn(SO_4)_3$, K_2. K for the reaction (1) was found to be 0.14 liters²/moles² and K_2 was found to be small. Electromigration studies were in agreement with the above reactions. At 1.5 f sulfuric acid the tin migrated to the cathode but at concentrations higher than 6 f H_2SO_4 it moves very slowly to the anode. Thus it appears that in 1 f to nearly 3 f sulfuric acid the tin(IV) ion is the predominant species. At higher sulfuric acid concentrations the tin (IV) sulfate is important. The trisulfato complex is present in substantial amounts only in very concentrated sulfuric acid.

In the course of an examination of the oxidation of tin(II) and reduction of tin(IV) in sulfuric acid it became necessary to obtain some information concerning the species of tin(IV) which might be present in this medium.

Ditte[2] has shown that stannic sulfate dihydrate ($Sn(SO_4)_2 \cdot 2H_2O$) can be prepared from approximately 1/4 sulfuric acid solution and Weinland and Kuhl[3] have prepared a series of $M_2Sn(SO_4)_3 \cdot nH_2O$ from concentrated sulfuric acid solutions of tin(IV).

Domange[4] found that chromous sulfate readily reduced tin(IV) in chloride solution, but not in sulfate, which might indicate the tin(IV) in sulfuric acid was cationic and the reaction was hampered by unfavorable coulombic effects (repulsion between Cr^{++} and the tin(IV) cation).

Spectrophotometric studies were undertaken, coupled with electromigration experiments, to determine whether further information concerning the nature of tin(IV) in sulfuric acid could be obtained.

Experimental.—Stannic hydroxide was prepared from an aqueous stannic chloride solution by precipitating the tin with ammonia solution. The stannic hydroxide thus obtained was repeatedly digested and washed with distilled water until no chloride ions could be detected in the washings. This precipitate was immediately dissolved in 1/8 sulfuric acid; the solution was hastened by warming on a steam-bath. The solution was then evaporated on the steam-bath until $Sn(SO_4)_2 \cdot 2H_2O$ began to crystallize. Further crystallization was brought about by cooling. The stannic sulfate dihydrate was then dissolved in approximately 2 f sulfuric acid and the solution was analyzed for tin and hydrogen ion. Duplicate determinations showed that the stock solution was 0.4117 f in tin and 4.483 N in sulfuric acid.

A solution of tin(IV) in perchloric acid was prepared by dissolving the chloride-free stannic hydroxide in approximately 3 N perchloric acid. Analyses showed that this solution was 0.2670 f in tin and 3.216 in perchloric acid.

Neither of the stock solutions was stable, since after a period of several weeks they became cloudy and finally white tin(IV) oxide precipitated. However, the dilute solutions described below were prepared before the stock solutions became turbid. The latter dilute solutions appear to be stable over the extended period of several months (at 25°).

Spectrophotometric examination of a series of tin(IV) sulfate and perchlorate solutions was carried out on a Beckman Model DU spectrophotometer, at 25° with quartz cells of path length 1.00 cm. and 0.100 cm. Since it was found that the extinction coefficients of the stannic ion and trisulfatostannate ion were large, the solutions, with varying amounts of sulfuric or perchloric acids, were prepared containing $1.647 \times 10^{-3} f$ tin. This was accomplished by mixing appropriate quantities of the stock solutions and standardized sulfuric or perchloric acid solutions.

Electromigration studies were carried out on one-half by ten inch strips of filter paper. The paper strips were suspended horizontally with the ends dipping into beakers containing sulfuric acid of the appropriate concentration.

Carbon electrodes were placed into each beaker and a regulated potential of 50 volts was applied across the electrodes. The paper was wet with the acid and a drop of a solution of tin(IV) in the same concentration of acid was placed in the center of the paper. After a period of six to eight hours the current was stopped and the spot was developed by playing a stream of hydrogen sulfide gas over the paper. A bell jar over the apparatus prevented evaporation and drying of the paper.

In Fig. 1 are shown some typical absorption spectra for tin(IV) in sulfuric acid and in perchloric acid solutions (in the range 200 to 300 mμ). The log of the "observed" extinction coefficient ($D_{obs}/C_{Sn}d$; where $D = \log I_0/I$ C_{Sn} is total tin(IV) and d is the cell path length in cm.) is plotted against wave length.

It will be seen that no clear cut maximum is observed in the region, so 240 mμ, which lies on the flat portion of the curves, was selected for the calculations.

In Table I are tabulated the values of D_{obs} for $1.65 \times 10^{-3} f$ tin in perchloric acid solutions of various concentrations. In Tables II and III are listed the data for $1.65 \times 10^{-3} f$ tin in various sulfuric acid solutions.

TABLE I[a]

THE OPTICAL DENSITY OF $1.65 \times 10^{-3} f$ Sn(IV) IN PERCHLORIC ACID SOLUTIONS

($HClO_4$), moles/l.	D_{obsd} (25°)	($HClO_4$), moles/l.	D_{obsd} (25°)
1.496	0.242	3.168	0.250
2.139	.236	5.901	.259
2.782	.254	8.752	.258
3.006	.248		

[a] Cell path = 0.100 cm.

Discussion.—Figure 2 shows e_{obs} at 240 mμ plotted against sulfuric acid concentration. The form of the first portion of this curve suggests the

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