tioned paper by the authors. Although these data are for the special case of $a - 2b = 0$, they have the advantage that the rate constants have been determined by an exact method.

Table I gives the values of x, t, Φ_i and θ_i.

TABLE I

RATE DATA FOR THE SAPONIFICATION OF ETHYL ADIPATE

a = initial concn. of sodium hydroxide = 0.00902 mole liter^{-1}. b = initial concn. of ethyl adipate = 0.00451 mole liter^{-1}

x = [NaOH] mole liter^{-1}	Time, seconds	$\Phi_i = \left(\frac{d \ln x}{dt}\right)_{t=t_i}$ seconds^{-1} $\times 10^{-4}$	$\theta_i = \int_0^{t_i} x dt$ liter^{-1} mole sec.
0.00902	0	−3.98	0
.00849	161		
.00808	309		
.00768	460		
.00724	655	−2.91	5.275
.00684	860		
.00650	1056		
.00604	1359	−2.32	9.922
.00565	1660		
.00531	1956		
.00501	2259	−1.83	14.863
.00468	2658		
.00431	3161		
.00401	3659	−1.42	21.122
.00374	4158		
.00352	4660		

The above information gives four equations of type (5). These equations were solved by elimination of k_2 between successive pairs of equations and the use of Newton's method.

Table II gives the values of k_1 and k_2 for the six possible cases.

TABLE II

k_1 liter mole^{-1} sec.$^{-1}$	k_2 liter mole^{-1} sec.$^{-1}$
0.0852	0.0309
.0857	.0301
.0850	.0312
.0870	.0297
.0849	.0312
.0812	.0318
Av. k_1 = 0.0848	Av. k_2 = 0.0308

The average values of k_1 and k_2 found by the exact method are

k_1 = 0.0855 liter mole^{-1} sec.$^{-1}$

k_2 = 0.0305 liter mole^{-1} sec.$^{-1}$

Conclusions

It is apparent that the numerical method used should be applicable to most two-step complex reactions. Further it can be used advantageously even in those cases where a closed form solution is known, since evaluation of rate constants is still a very tedious process in these cases.

Perhaps the chief disadvantage of the method is that rather precise data are necessary since values of k_1 and k_2 were found to be very sensitive to small errors in θ_i and Φ_i.

LINCOLN 8, NEBRASKA RECEIVED FEBRUARY 26, 1951

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, STANFORD UNIVERSITY]

Four Mechanisms Involving Nitrogen Pentoxide

BY HAROLD S. JOHNSTON

The mechanisms of four kinetic systems involving nitrogen pentoxide can be expressed in terms of eight reactions which are believed to be elementary steps. The central feature of these mechanisms is a rapidly attained equilibrium between nitrogen pentoxide and nitrogen dioxide and NO_3. In terms of the mechanism quantitative relations are found among the four systems. From experimental data plus two additional assumptions, seven out of eight rate constants and the equilibrium constant can be evaluated within one order of magnitude. The steady-state concentration of NO_3 can be estimated for each kinetic system. Approximate values of the energy of activation can be found for five of the eight steps.

Four complex kinetic systems, some of which have been extensively investigated, can be expressed in terms of eight processes which are believed to be elementary reactions. Some of these eight steps occur in all four mechanisms, and thus quantitative relations are to be sought between them.[1] The four kinetic systems are: (1) The decomposition of nitrogen pentoxide, (2) the decomposition of nitrogen pentoxide in the presence of nitric oxide, (3) the decomposition of ozone in the presence of nitrogen pentoxide, and (4) the formation of nitrogen pentoxide from ozone and nitrogen dioxide. The eight elementary steps are

$$N_2O_5 + M \xrightarrow{a_{iM}} N_2O_{5i}^* + M$$

$$N_2O_{5i}^* + M \xrightarrow{b_{iM}} N_2O_5 + M$$

$$N_2O_{5i}^* \xrightarrow{c_i} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{d_i} N_2O_{5i}^*$$

$$NO_2 + NO_3 \xrightarrow{e} NO + O_2 + NO_2$$

$$NO + NO_3 \xrightarrow{f} 2NO_2$$

$$NO_3 + NO_3 \xrightarrow{g} 2NO_2 + O_2$$

$$NO_2 + O_3 \xrightarrow{h} NO_3 + O_2$$

The asterisk denotes excitation, and the subscript i numbers the excited states of the nitrogen pentoxide above the critical energy. M denotes any gas molecule which contributes to the excitation and de-excitation of nitrogen pentoxide. The subscript M on the specific rate constants is necessary because the excitation and de-excitation rates depend on the nature of the gas M as well as on its concentration. If all gases are equally

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[1] H. S. Johnston, *The Vortex* **9**, 356 (1948); Thesis, Calif. Inst. of Tech., 1947.

effective or if any one gas is present in great excess, the subscript M could be dropped. The second-order rate constants are written without subscript, for in analysis of mechanism it makes no difference whether one writes e or $\sum_j e_j$; there is no way to decompose the sum over excited states of the activated complex. For unimolecular reactions, however, even in analysis of mechanism it makes great difference whether one writes $\frac{ac[\mathrm{M}]}{b[\mathrm{M}] + c}$ or $\sum_i \frac{a_i c_i[\mathrm{M}]}{b_i[\mathrm{M}] + c_i}$ for the first-order rate constant. Here the more cumbersome yet essential second formulation is used.

Equilibrium of Nitrogen Pentoxide

These mechanisms are based on the assumption of a rapidly attained equilibrium

$$N_2O_5 \rightleftarrows NO_2 + NO_3$$

This equilibrium was considered and rejected by Schumacher and Sprenger,[2] but was re-considered by Smith and Daniels[3] and by Ogg.[4] The unification it gives to these four reaction mechanisms justifies its serious examination at this time. In the absence of the irreversible reactions e, f and g, the mechanism for the two opposing reactions is given by a, b, c and d. The equilibrium constant K derived from this mechanism is

$$K = \frac{[NO_2][NO_3]}{[N_2O_5]} = \frac{A(M)}{B(M)}$$
$$= \frac{\sum\limits_i \frac{\sum\limits_M a_{iM} c_i[\mathrm{M}]}{\sum\limits_{\mathrm{M}} b_{iM}[\mathrm{M}] + c_i}}{\sum\limits_i \frac{\sum\limits_M b_{iM} d_i[M]}{\sum\limits_M b_{iM}[\mathrm{M}] + c_i}} \tag{1}$$

where (M) indicates functional relationship, [M] stands for concentration and $A(M)$ and $B(M)$ are abbreviations for the numerator and denominator of the last expression. Evidence will be pointed out below to the effect that K is independent of [M] above 0.1 mm.

Reaction (1). The Decomposition of Nitrogen Pentoxide.—This mechanism was first proposed and later extended by Ogg.[4,5] The mechanism was elaborated explicitly to include the variable [M] and put in the sum-over-excited-states form by Mills and Johnston.[6] The present treatment also recognizes that the constants a and b depend on the nature of gases M and explicitly sums over all different gases. The mechanism is given by steps a, b, c, d, e, and f. The steady-state assumptions are made for NO_3 and the excited states of nitrogen pentoxide, $N_2O_{5i}{}^*$. The rate is expressed as the rate of appearance of nitrogen dioxide (assuming that appropriate corrections have been made for nitrogen tetroxide).

$$R = \frac{\mathrm{d}[NO_2]}{\mathrm{d}t} = \frac{[N_2O_5]\,\{e + 3f[NO]/[NO_2]\}\,A(M)}{e + f[NO]/[NO_2] + B(M)} \tag{2}$$

If no nitric oxide is added from the outside and if no side reaction produces nitric oxide, the steady state assumption, $e[NO_2] = f[NO]$, may be made for nitric oxide also which gives

$$R^{(1)} = \frac{\mathrm{d}[NO_2]}{\mathrm{d}t} = \frac{2[N_2O_5]A(M)}{1 + B(M)/2e} \tag{3}$$

If a given foreign gas is present in very large excess or if only pure reactant (initial condition) is present, only one species M needs to be considered, and Equation 3 reduces to Equation 13 of Mills and Johnston,[6] who have analyzed it in detail with respect to high and low limits. At all concentrations where $B(M) \gg 2e$ the empirical first-order rate constant defined by $-\mathrm{d}[N_2O_5]/\mathrm{d}t = k^{(1)}[N_2O_5]$ is according to the mechanism

$$k^{(1)} = 2eK \tag{4}$$

The fact that the rate constant for the decomposition of nitrogen pentoxide is independent of concentration above 0.1 mm. implies that the equilibrium constant K is independent of concentration over this range which extends from the low-pressure to the high pressure limit[6] of the unimolecular reaction a, b and c. At high concentrations where $b_i[\mathrm{M}] \gg c_i$ for all i, the rate constant is

$$k_\infty{}^{(1)} = \frac{2e\sum\limits_i a_i c_i/b_i}{d} \tag{5}$$

where $d = \sum\limits_i d_i$. At extremely low concentrations where $b_i[\mathrm{M}] \ll c_i$ for all i and also where $B(M) \ll 2e$, the first-order rate constant divided by total concentration [M] gives the second-order rate of activation

$$\frac{k_0{}^{(1)}}{[\mathrm{M}]} = \sum_i a_i = a \tag{6}$$

The steady-state concentration of NO_3 is

$$[NO_3]^{(1)} = \frac{[N_2O_5]\,A(M)}{[NO_2]\,[B(M) + 2e]} \approx \frac{K[N_2O_5]}{[NO_2]} \tag{7}$$

The approximation is valid above 0.1 mm. total pressure.

Reaction (2). The Decomposition of Nitrogen Pentoxide in the Presence of Nitric Oxide.—This mechanism was proposed by Smith and Daniels.[3] It was extended to include foreign gases and expressed as sum-over-excited-states by Mills and Johnston.[6] This treatment generalizes it with respect to different varieties of gases M.

If excess nitric oxide is added to the system so that $f[NO] \gg e[NO_2]$, Equation 2 above reduces to

$$\frac{\mathrm{d}[NO_2]}{\mathrm{d}t} = \frac{3\,[N_2O_5]\,A(M)}{1 + (M)\,[NO_2]/f[NO]} \tag{8}$$

If the sum over M is dropped from $A(M)$ and $B(M)$, this expression becomes the same as Mills and Johnston's Equation 7. Defining the rate constant in terms of nitrogen pentoxide, $-\mathrm{d}[N_2O_5]/\mathrm{d}t = k^{(2)}[N_2O_5]$, the factor of three drops out of Equation 8. The high-concentration limit of the initial rate of reaction gives

$$k_\infty{}^{(2)} = \sum_i \frac{a_i c_i}{b_i} \tag{9}$$

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[2] H. J. Schumacher and G. Sprenger, *Z. physik. Chem.*, **140**, 281 (1929).

[3] J. H. Smith and F. Daniels, This Journal, **69**, 1735 (1947).

[4] R. A. Ogg, Jr., *J. Chem. Phys.*, **15**, 337, 613 (1947).

[5] R. A. Ogg, Jr., *ibid.*, **18**, 572 (1950).

[6] R. L. Mills and H. S. Johnston, This Journal, **73**, 938 (1951).

and the low-concentration limit is

$$\frac{k_0^{(2)}}{[\mathrm{M}]} = \sum_i a_i = a \qquad (10)$$

The steady-state concentration of NO_3 is

$$[\mathrm{NO_3}]^{(2)} = \frac{[\mathrm{N_2O_5}]\,A(M)}{[\mathrm{NO_2}]\,B(M) + f[\mathrm{NO}]} \approx \frac{[\mathrm{N_2O_5}]\,A(M)}{f[\mathrm{NO}]} \qquad (11)$$

Equation 2 given above should describe in detail[7] the complex curves shown by Smith and Daniels[3] in their Fig. 3 wherein the rate of appearance of nitrogen dioxide changes suddenly from the fast rate with nitric oxide to the much slower rate characteristic of nitrogen pentoxide alone. Sensitive simultaneous measurement of both nitric oxide and nitrogen dioxide over such runs at high concentration of foreign gas M would give the ratio of the elementary rate constants f/d.

Reaction (3). The Decomposition of Ozone in the Presence of Nitrogen Pentoxide.—The mechanism usually accepted for the nitrogen pentoxide catalyzed decomposition of ozone is due to Schumacher and Sprenger.[8] A later mechanism by Sprenger[9] gives the observed rate law in a direct manner and free from the algebraic difficulties of the older mechanism. Sprenger's mechanism is the one accepted and extended here. It is given by steps a, b, c, d, h and g. Steady state assumptions are made for $[NO_3]$, $[NO_2]$, $[N_2O_{5i}^*]$ and $[N_2O_5]$. From this mechanism and these steady state assumptions there follows directly and exactly the complex rate expression

$$-\mathrm{d}[\mathrm{O_3}]/\mathrm{d}t = h^{2/3}\,(2g)^{1/3}K^{2/3}[\mathrm{N_2O_5}]^{2/3}[\mathrm{O_3}]^{2/3} \qquad (12)$$

and the empirical rate constant is

$$k^{(3)} = h^{2/3}(2g)^{1/3}K^{2/3} \qquad (13)$$

This four-thirds order rate law was observed,[8] and the concentration of both nitrogen pentoxide and ozone was varied over a considerable range.

The steady-state concentration of NO_3 is given by

$$[\mathrm{NO_3}]^{(3)} = (hK/2g)^{1/3}[\mathrm{N_2O_5}]^{1/3}[\mathrm{O_3}]^{1/3} \qquad (14)$$

The optical density due to NO_3 was observed by Sprenger[9] to depend on nitrogen pentoxide and ozone each to the one-third power. From Equations 14 and 12 it can be seen that

$$-\mathrm{d}[\mathrm{O_3}]/\mathrm{d}t = 2g\{[\mathrm{NO_3}]\}^2 \qquad (15)$$

The steady state concentration of nitrogen dioxide is

$$[\mathrm{NO_2}]^{(3)} = (2g/h)^{1/3}\{K[\mathrm{N_2O_5}]\}^{2/3}/[\mathrm{O_3}]^{1/3} \qquad (16)$$

No absorption bands[9] due to nitrogen dioxide could be found in this system.

Reaction (4). Formation of Nitrogen Pentoxide from Ozone and Nitrogen Dioxide.—This mechanism was predicted by Schumacher and Sprenger[2] and proposed to explain observed rates by Johnston and Yost.[10] This mechanism is given by h, d, c and b. The over-all reaction is so fast that other steps need not be considered. Assuming steady-state conditions for $[N_2O_{5i}^*]$ and $[NO_3]$, the rate expression is simply

$$-\mathrm{d}[\mathrm{O_3}]/\mathrm{d}t = h[\mathrm{NO_2}][\mathrm{O_3}] \qquad (17)$$

and the empirical rate constant is

$$k^{(4)} = h \qquad (18)$$

The steady-state concentration of NO_3 is

$$[\mathrm{NO_3}]^{(4)} = h[\mathrm{O_3}]/B(M) \qquad (19)$$

Relations between Kinetic Systems.—The empirical rate constants for the four kinetic systems are listed in Table I with the reference to the experimental results. No effort was made to include all measured rate constants, but rather it is intended to present the latest or the best results. The rate constants are interpolated to 27° for reactions (3) and (4), and extrapolated 8° to 27° for reaction (1) at low pressures.

TABLE I

OBSERVED VALUES OF EMPIRICAL RATE CONSTANTS AND ENERGIES OF ACTIVATION

Empirical rate constant	Value at 27°	Energy of activation, kcal.	Reference
$k_0^{(1)}/[\mathrm{N_2O_5}]$	1.5×10^5 cc. mole^{-1} sec.$^{-1}$	20.8 ± 2	11, 13
$k_\infty^{(1)}$	8.2×10^{-5} sec.$^{-1}$	24.7 ± 0.1	12
$k_0^{(2)}/\{[\mathrm{NO}] + [\mathrm{N_2O_5}]\}$	1.27×10^5 cc. mole^{-1} sec.$^{-1}$	19.3 ± 0.6	13
$k_\infty^{(2)}$	0.29 sec.$^{-1}$	21 ± 2	6
$k^{(3)}$	0.026 (cc./mole)$^{-1/3}$ sec.$^{-1}$	20.5 ± 1	9
$[\mathrm{NO_3}]^{(3)}$	....	6.2 ± 0.8	9
$k^{(4)}$	4.7×10^7 cc. mole^{-1} sec.$^{-1}$	7.0 ± 0.6	10

The best extremely low-pressure work on system (1) seems to be that of Linhorst and Hodges.[11] For high-pressure rate constants of the decomposition of nitrogen pentoxide, the best work seems still to be that of Daniels and Johnston.[12] The low-pressure study of reaction (2) by Mills and Johnston[6] has been found to be partly heterogeneous by Johnston and Perrine,[13] whose data are used in Table I. The magnitude of the heterogeneous reaction is entirely negligible at high pressures, and thus Mills and Johnston's data are used there. The data for the third system are those of Sprenger.[9] The rate constant for reaction (4) is that of Johnston and Yost.[10] Sprenger[9] observed the temperature coefficient of the optical density of NO_3 in system (3). The average (for two different wave lengths) "energy of activation" of the steady state concentration was found and is listed in Table I. Thus Table I contains nothing but empirical rate constants and energies of activation taken directly from the literature.

Table II, on the other hand, is built around the assumed mechanisms, but it involves no additional assumptions. According to the mechanisms one can multiply and divide the empirical rate constants in Table I to give several ratios of elementary rate constants, and by adding and subtracting the corresponding energies of activation one can get the energy of activation of these ratios. The energy of activation of reaction (3) minus twice the energy term for the steady state concentration of NO_3 gives the energy of activation of step g. Only two of the eight rate constants are observed directly, a and h, and no other single-step constants

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[7] Private communication from Yu-sheng Tao.

[8] H. J. Schumacher and G. Sprenger, *Z. physik. Chem.*, **2B**, 266 (1929).

[9] G. Sprenger, *Z. Elektrochem.*, **37**, 674 (1931).

[10] H. S. Johnston and D. M. Yost, *J. Chem. Phys.*, **17**, 386 (1949).

[11] E. F. Linhorst and J. H. Hodges, THIS JOURNAL, **56**, 836 (1934).

[12] F. Daniels and E. H. Johnston, *ibid.*, **43**, 53 (1921).

[13] H. S. Johnston and R. L. Perrine, *ibid.*, **73**, in press (1951).

can be separated from the deduced ratios. However, if one found a precise value of either d, e, g, K, or the optical extinction coefficient of NO_3, one could evaluate from known ratios all other members of the set. It is desirable to measure two or more of these quantities separately in order to provide checks on these mechanisms. In the absence of further assumption, the present state of knowledge on these four mechanisms is summarized in Table II.

TABLE II

ELEMENTARY RATE CONSTANTS, RATIOS OF RATE CONSTANTS, AND OTHER QUANTITIES DERIVED FROM THE MECHANISMS AND DATA IN TABLE I

In terms of these mechanisms		Numerical values computed from Table I		
Expression	Eqns. in text comb. to get expression	Value at 27° in units of moles, cc., sec.	Empirical rate constants combined to get the values	Energy of activation, kcal.
$a(N_2O_5)$	6	1.5×10^5	$k_0{}^{(1)}$	20.8 ± 2
$a(NO + N_2O_5)$	10	1.27×10^5	$k_0{}^{(2)}$	19.3 ± 0.6
$\sum_i a_i c_i / b_i$	9	0.29	$k_\infty{}^{(2)}$	21 ± 2
eK	4	4.1×10^{-5}	$k_\infty{}^{(1)}$	24.7 ± 0.1
d/e	5, 9	7×10^3	$k_\infty{}^{(2)}, k_\infty{}^{(1)}$	-4 ± 2
f/d	8	>10	Ref. 6	....
h	18	4.7×10^7	$k^{(4)}$	7.0 ± 0.6
$g^{1/2}K$	13, 18	6.0×10^{-11}	$k^{(3)}, k^{(4)}$	24 ± 2
g	15, 12	....	Ref. 9	8.1 ± 2

By making two additional assumptions the ratios in Table II can be broken down to give some numerical information about all eight rate constants of the steps in the mechanism. The first assumption is that of the collisional theories of unimolecular reactions.[14,15] This group of theories usually employs the assumption that essentially every collision of an excited molecule results in energy redistribution and thus the loss of the excited molecule. For critical energies very much larger than the ground vibrational energy, the assumption appears reasonable. The result is: $b_i = b =$ kinetic theory collision constant $\approx 1 \times 10^{14}$ cc. mole^{-1} sec.$^{-1}$ for normal simple gas molecules. This assumed value is listed in Table III. Next the average value of c_i or $\bar{c}$ can be found, since by Equations 9 and 10

$$\frac{b\,k_\infty{}^{(2)}}{k_0{}^{(2)}} = \frac{\sum_i a_i\, c_i}{\sum_i a_i} = \bar{c} = 2 \times 10^8 \text{ sec.}^{-1} \qquad (20)$$

Detailed values of the specific rate constants c_i might be found from an examination of the function log $k^{(2)}$ *vs.* log [M], but this analysis has not yet been made.

The next assumption, which permits evaluation to plus or minus one order of magnitude of the other elementary rate constants (*except f*) is an extremely crude one, and the error may be much larger than the estimated probable error. In Table II the energy of activation of step g was given as 8.1 ± 2 kcal. Our experience (3 cases) in this Laboratory with very fast bimolecular reactions, having energies of activation below 10 kcal., is that the pre-exponential factors are between 10^{12} and 10^{13} cc. mole^{-1} sec.$^{-1}$. Thus in terms of the collision theory of bimolecular reactions, a "steric factor" of 0.01 was assigned to step g; or in other words the pre-exponential term was assumed to be 1×10^{12} cc. mole^{-1} sec.$^{-1}$. Thus g is provisionally evaluated, and it is listed in Table III. From Table II it is seen that the known combination is $g^{1/2}K$; thus errors in g are reduced by taking the square root. The other chain of calculations are: K is evaluated from $g^{1/2}K$; e is found from eK; d is given by the ratio d/e; and the limit is set on f from the known limit on f/d. The magnitude of rate constant a can be accounted for in terms of about 10 oscillators.[13] All other second order rate constants can be accounted for in terms of collision frequencies. There is no knowledge from other experiments or *a priori* which contradicts the values in Table III.

TABLE III

ELEMENTARY RATE CONSTANTS DERIVED FROM TABLE II PLUS TWO ADDITIONAL ASSUMPTIONS

Quantity	Value at 27°C. cc. mole^{-1} sec.$^{-1}$ unless noted	Source in terms of Tables II and III	Pre-exponential factor	Energy of activation, kcal.
a	1.27×10^5	a	1.3×10^{19}	19.3 ± 0.6
b	1×10^{14}	Theory	....	....
$\bar{c}$	2×10^8 sec.$^{-1}$	b, $\Sigma ac/b$, a	....	....
d	4×10^{12}	d/e, e	2×10^{13}	1 ± 4
e	7×10^8	eK, K	4×10^{12}	5 ± 3
f	$>10^{13}$	f/d, d	....	....
g	1×10^6	Assumed steric factor	1×10^{12}	8.1 ± 2
h	4.7×10^7	h	5.9×10^{12}	7.0 ± 0.6
K	6×10^{-14} mole cc.$^{-1}$	$g^{1/2}K$, g	....	20 ± 3

The rate constants in Table III were used to calculate the steady-state pressure at 27° of NO_3 in each of the four kinetic systems. All reactants, catalysts, and final products were assumed to be present at 10^{-5} mole cc.$^{-1}$ or at 187 mm. partial pressure, and the total pressure is one atmosphere. These steady-state pressures are listed in Table IV. It is thus clear why NO_3 has not been observed in reaction (1) and (2) at room temperature, even though the mechanism calls for its steady-state presence. However, Ogg and Weston[16] report the presence of the characteristic absorption spectrum of NO_3 in a flow system at high temperature.

TABLE IV

STEADY STATE PRESSURE AT 27° OF NO_3 IF ALL REACTANTS, CATALYSTS, AND FINAL PRODUCTS ARE PRESENT AT 187 MM. PARTIAL PRESSURE

Kinetic system	Steady-state pressure, mm.	Remarks	Reference
1	10^{-6}	Looked for, not found	8
2	$<10^{-8}$	Looked for, not found	3
3	1	Observed	8, 9
4	0.005	....	...

These eight steps are sufficient to account for the observed homogeneous phenomena of these four complex kinetic systems. The prediction that the second order rate of activation of system (1) and (2) becomes the same (except for the slight

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[14] R. C. Tolman, "Statistical Mechanics," Chemical Catalog Co., (Reinhold Publ. Corp.), New York, N. Y., 1927, Chap. 21.

[15] L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., (Reinhold Publ. Corp.), New York, N. Y., 1932, pp. 98–99.

[16] Ralph Weston, Thesis, Stanford University, 1950.

difference in what constitutes [M] in each case) has been confirmed[13] over a wide temperature range. The prediction of the pressure at which the first rate constant "falls off" has been confirmed.[6,13] The values of the elementary rate constants in Table III are reasonable. The calculated steady-state pressures of NO_3 agree qualitatively with observations which are themselves qualitative. Thus these mechanisms are probably as well-established as any complex mechanism in chemical kinetics.

Further work is needed on these systems. It is particularly desirable to have independently measured values of K, the extinction coefficient of NO_3, and the ratio f/d. These three quantities appear to be more nearly available experimentally than the absolute values of the bimolecular rates involving NO_3.

STANFORD, CALIFORNIA RECEIVED FEBRUARY 10, 1951

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

Rate Law and Mechanism of the Reaction of Iodine with Tetrathionate Ion

BY ALICE D. AWTREY AND ROBERT E. CONNICK

The kinetics of the oxidation of tetrathionate ion to sulfate by iodine was investigated under two widely different sets of conditions. The rate law was found to be $-\,d(\Sigma I_2)/dt = k_4(S_4O_6^=)(I_2)/(I^-)$ in both cases, although the value of k_4 differed by approximately a factor of two. The following mechanism is proposed: $S_4O_6^= + I_2 \rightleftarrows S_4O_6I^- + I^-$, then $S_4O_6I^- \rightarrow$ where the first reaction is a rapid equilibrium shifted far to the left and the second is the rate-determining step. It is proposed that the factor of two variation in k_4 arises from a change in the reactions following the rate-determining step. The heat and entropy of activation are 26 kcal. and 9 e.u., respectively.

Introduction

The rate of reaction of tetrathionate ion with iodine was studied in connection with the investigation of the thiosulfate–iodine reaction.[1] The oxidation of tetrathionate by iodine in acid solution seems to have been mentioned only once in the older literature. C. A. R. Wright[2] reported that, if an excess of iodine solution was left standing with thiosulfate overnight, a considerable amount of iodine disappeared, though volatilization of the iodine was prevented, and he showed that sulfate ion was produced.

$$S_4O_6^= + 7I_2 + 10H_2O = 4SO_4^= + 14I^- + 20H^+ \qquad (1)$$

While the present work was in progress, Dodd and Griffith[3] published preliminary results of a study of this system.

Experimental

$Na_2S_4O_6 \cdot 2H_2O$.—The salt was prepared from iodine and sodium thiosulfate, as described in the literature.[4] Analysis gave 12.72% H_2O, and 41.54% S. Calculated values for $Na_2S_4O_6 \cdot 2H_2O$ are 11.76% H_2O, 41.87% S, molecular weight 306.3. If the solid has 12.72% H_2O, then the calculated per cent. S is 41.41, which is the observed within experimental error, and the molecular weight is 309.6. This value for the molecular weight was used. Qualitative tests[5] showed a trace of sulfate, no iodide, no trithionate nor pentathionate.

Solutions.—Approximately 10^{-3} M tetrathionate solutions were made up by weight, and diluted for use in the experiments. In general, the stock solutions were not used more than a week after being prepared. The dry salt is stable, but solutions have a measurable rate of decomposition.[5]

All chemicals other than the tetrathionate were reagent-grade. Sodium perchlorate solutions were prepared by neutralization of perchloric acid with sodium carbonate. Distilled water, redistilled from alkaline permanganate solution, was used in making up all solutions.

The concentrations of iodine and triiodide solutions were determined either by titration of the stock solutions with standardized thiosulfate, or spectrophotometrically.

Either hydrochloric or perchloric acid was used, and potassium chloride was added to give the desired ionic strength. Allowance was made in all calculations for the formation of I_2Cl^-.[1] All concentrations are expressed in moles per liter of solution indicated by M.

Procedure.—There were two kinds of experiments. The first had iodide and tetrathionate in large excess, so that their concentrations were constant, and the decrease in triiodide concentration was followed as a function of time. The second had no iodide added, and a slight excess of iodine over tetrathionate, so that the concentrations of all the reactants changed greatly during an experiment.

For the first kind the reaction was slow; the tetrathionate was pipetted into a solution of the other reactants, the mixture shaken and an absorption cell filled. The reaction was followed by measuring the triiodide concentration with a Beckman spectrophotometer, using a thermostated cell-holder.

For the second type, a solution of tetrathionate and potassium chloride (or sodium perchlorate) was mixed with one containing iodine and acid, by means of the small mixing device previously described.[1] The reaction was followed spectrophotometrically by measuring the optical density at both the iodine and triiodide maxima. Using the molar extinction coefficients given in Table I, the I_2 and I_3^- concentrations were calculated; from these and the triiodide equilibrium constant[1,6] the iodide ion concentration was determined. The total iodide, *i.e.*,[8] $(\Sigma I^-) = (I^-) + (I_3^-)$, is a measure of the amount of tetrathionate that has reacted, since no iodide was added

TABLE I

MOLAR EXTINCTION COEFFICIENTS FOR I_2, I_3^- AND I_2Cl^-

Wave length, Å.	ϵ_{I_2}	$\epsilon_{I_3^-}$	$\epsilon_{I_2Cl^-}$[7]
4600	746	975	880
3530	19	26400	235

$$(S_4O_6^=) = (S_4O_6^=)_0 - (\Sigma I^-)/14 \qquad (2)$$

A check was made on the accuracy of the calculation of the iodine, triiodide and iodide concentration by calculating the total iodine in the solution

$$(\Sigma I) = (I^-) + 3(I_3^-) + 2(I_2) + 2(I_2Cl^-) \qquad (3)$$

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[1] A. D. Awtrey and R. E. Connick, THIS JOURNAL, **73**, 1341 (1951).

[2] C. A. R. Wright, *Chem. News*, **21**, 103 (1870).

[3] G. Dodd and R. O. Griffith, *Trans. Faraday Soc.*, **45**, 546 (1949).

[4] Abegg and Auerbach, "Handbuch der anorg. Chem.," Vol. 4, 1927, p. 554.

[5] Yost and Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, pp. 395, 397.

[6] G. Jones and B. B. Kaplan, THIS JOURNAL, **50**, 1845 (1928).

[7] A. D. Awtrey and M. S. Tsao, to be published.

[8] Parentheses are used to designate concentrations in moles per liter.