HCN = $(HCN)_{n+1}$ with the same equilibrium constant

$$K = C_{n+1}/C_nC_1 \qquad (1)$$

for all, where C_n is the concentration of n-mer. If C_0 is the gross concentration as monomer, one obtains the well-known equilibrium expression

$$C_1/(1 - KC_1)^2 = C_0 \qquad (2)$$

The dielectric constant ϵ in Kirkwood's theory is related to the dipole moment μ_0 of the free molecule by the expression

$$\epsilon = \epsilon_\infty + \frac{3\epsilon}{2\epsilon + \epsilon_\infty}\left(\frac{\epsilon_\infty + 2}{3}\right)^2 \frac{4\pi N}{3kTV} g\mu_0^2 \qquad (3)$$

where ϵ_∞ is the dielectric constant for induced polarization, N, kT and V have their usual meaning, and the factor $g\mu = g(\epsilon_\infty + 2)\mu_0/3$ is the average moment of the single molecule and its local environment. In the simplified model, this is the average over values $n\mu$, for each molecule of an n-unit straight chain, weighted by the number nC_n of such molecules. This gives

$$g\mu = (\mu/C_0)\sum_{n=1}^{\infty} n^2C_n = \mu\frac{1 + KC_1}{1 - KC_1}$$

on using (1) for the C_n. From eq. 2, one then has

$$KC_0 = (g^2 - 1)/4 \qquad (4)$$

From this result, equilibrium constants KC_0 can be calculated for "experimental" correlation factors g obtained by using measured values of dielectric constant and dipole moment in eq. 3. Using μ_0 = 2.96 debye and dielectric constant data from reference 2 gives the values in Table I.

TABLE I

DIELECTRIC CONSTANT AND ASSOCIATION PARAMETERS

t, °C.	−13.3	−5	5	15	25.7
	(f.p.)				(b.p.)
ϵ	205.5	173.7	144.8	123.5	105.7
g^a	4.04	3.52	3.04	2.68	2.38
KC_0	15.6	11.4	8.26	6.20	4.65

[a] Calculated using ϵ_∞ = 1.60 and molar volume V = 39.8 cm.³.

The model may be tested by a rate plot of log KC_0 *versus* reciprocal temperature, which should give a straight line with a reasonable heat of association from the slope. This plot is shown in Fig. 1, and the slope of the straight line corresponds to the figure ΔH = −4.6 kcal./mole. This is interestingly close to the values 3.3 and 4.4 kcal./mole deduced by Long, Hildebrand and Morrell[4] for dimer and trimer formation in the vapor phase. The results are, however, not immediately comparable because of the difference in molecular environment and our simplifying assumption of identical equilibrium expressions for all degrees of association. Such refinements as including a distinct constant for dimers, which have been made in analyzing infrared absorption of alcohol solutions,[5] hardly seem warranted in view of the other approximations in the dielectric constant expression (3) and association model employed.

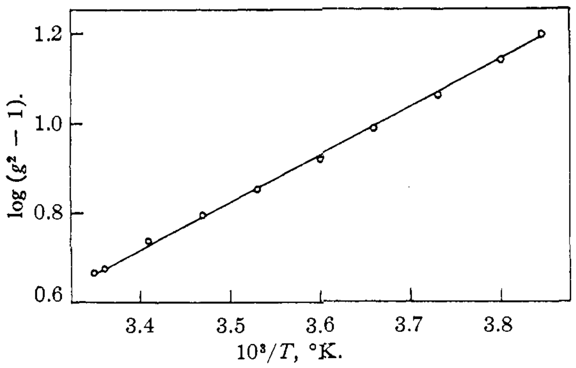

Fig. 1.—Correlation function from eq. 4 as a function of reciprocal temperature.

The temperature dependence of the dielectric constant is thus satisfactorily represented by the model, which is naturally inferred from the known arrangement of parallel linear chains in the solid. The regular arrangement of chains in the solid is not expected or assumed for the liquid; rather, the treatment is a simplified representation of fluctuating directed coördinations by hydrogen bonds of otherwise randomly oriented molecules. A similar discussion of hydrogen bonding in pure alcohols by an extension of Oster and Kirkwood's development[6] to include finite extent of molecular correlation gives a simple basis for understanding variations in the magnitude and temperature dependences of the dielectric constants for different aliphatic alcohols. This analysis will be presented elsewhere.

Acknowledgment.—This work was part of a program supported by the Office of Ordnance Research.

[4] R. W. Long, J. H. Hildebrand and W. E. Morrell, THIS JOURNAL, **65**, 182 (1943).

[5] N. D. Coggeshall and E. L. Saier, *ibid.*, **73**, 5414 (1951).

[6] G. Oster and J. G. Kirkwood, *J. Chem. Phys.*, **11**, 175 (1943).

METCALF CHEMICAL LABORATORIES
BROWN UNIVERSITY
PROVIDENCE, RHODE ISLAND

Methods of Obtaining Rate Constants for Reactions of Half Order and of Mixed Half Plus First Order Followed Manometrically

BY DELOS F. DETAR

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In the course of manometric studies of the rates of the thermal decomposition of benzenediazonium salts in methanolic solutions in the presence of acetate buffers, complex pressure–time curves were obtained.[1] Most of these reactions proved to be of half order, of first order, or of mixed half plus first order. A number of methods of treating these data were investigated from the standpoint of convenience, accuracy and evidence of correctness of the assumed kinetic order. The most reliable method was found to be the least squares procedure. Useful first approximations to the constants of reactions of mixed half plus first order can be obtained graphically.

Equation 1 is the differential expression for a reaction of mixed half plus first order.

[1] D. F. DeTar and M. N. Turetzky, in preparation.

$$\mathrm{d}p/\mathrm{d}t = k_1(p_\infty - p) + k_{1/2}(p_\infty - p)^{1/2} \qquad (1)$$

$$\ln (y_0 + k_{1/2}/k_1)/(y + k_{1/2}/k_1) = k_1t/2$$

$$y = (p_\infty - p)^{1/2},\ y_0 = (p_\infty - p_0)^{1/2} \qquad (2)$$

$$p = a + be^{ct} + de^{2ct} \qquad (3)$$

$$a = p_\infty - (k_{1/2}/k_1)^2,\ d = -[(p_\infty - p_0)^{1/2} + k_{1/2}/k_1]^2,$$

$$b = (2k^{1/2}/k_1)\ [(p_\infty - p_0)^{1/2} + k_{1/2}/k_1],\ c = -k_1/2$$

and $k_1 = -2c,\ k_{1/2} = -cb/(-d)^{1/2},\ p_\infty = a - b^2/(4d)$

This integrates to eq. 2, which can in turn be rearranged to give eq. 3. Nozaki and Bartlett[2] developed a method for obtaining rate constants for a reaction of mixed first plus three halves order, and the same principle can be applied to eq. 2. The procedure is to carry out two reactions using different y_0 values but with the same set of t values for each. Since the series of $k_1t_i/2$ values is the same for both reactions, the t term can be eliminated and logs removed to give eq. 4, y_0 and y referring to one

$$(k_1y_0 + k_{1/2})/(k_1y + k_{1/2}) = (k_1y_0' + k_{1/2})/(k_1y' + k_{1/2}) = q \qquad (4)$$

reaction and y_0' and y' referring to the second reaction. Equation 4 rearranges to eq. 5; and a plot of y *vs.* y' gives a straight line with $k_{1/2}/k_1$ equal to

$$y = qy' + (k_{1/2}/k_1)(q - 1) \qquad (5)$$

the intercept divided by the (slope -1). By eq. 2 a plot of $\ln(y + k_{1/2}/k_1)$ *vs.* t gives a straight line of slope $k_1/2$.

For reactions followed manometrically, volumetrically or dilatometrically there is a convenient way to get both the y and the y' values from a single run. Pressure readings are obtained at t_1 and t_1', t_2 and t_2', etc., with $t_i - t_i'$ constant; pressure readings at $t_1, t_2, t_3 \ldots t_i$ are used in calculating y values for the "first reaction" and pressure readings at $t_1', t_2' \ldots t_i'$ are used for the corresponding "second reaction" y' value calculations. Usually the t_i' readings conveniently refer to the last 15–25% of the reaction and the t_i readings to the first part of the reaction. Unfortunately, the $k_{1/2}/k_1$ ratio is sensitive to errors in the slope and in the intercept and the above method is not very accurate.

Somewhat better results are obtained from the differential equation (eq. 1) used in the form given in eq. 6 by plotting the left-hand side against

$$(\mathrm{d}p/\mathrm{d}t)/(p_\infty - p)^{1/2} = k(p_\infty - p)^{1/2} + k^{1/2} \qquad (6)$$

$(p_\infty - p)^{1/2}$ to give a straight line with slope k, and intercept $k_{1/2}$. The problem with this method is to obtain sufficiently accurate values of $\mathrm{d}p/\mathrm{d}t$. Graphical methods give rather erratic results. Numerically[3] $\mathrm{d}p/\mathrm{d}t = (1/\tau)[\Delta^1p - (^1/_2)\Delta^2p + (^1/_3)\Delta^3p - \ldots]$ where Δ^1p refers to the first differences of a table of p values taken at even intervals (τ) of time, Δ^2p is the second difference and Δ^3p is the third difference. Applications of this formula to data smoothed by the method of Whittaker and Robinson[3] using $\epsilon = 1$ gave suitable values of $\mathrm{d}p/\mathrm{d}t$ for plotting. This method is illustrated in Table I; a plot of the values in col. 6 against those in col. 5 gives a line of slope 0.0315 and intercept 0.341. These values may be compared with the least squares values $k_1 = 0.0298$ and $k_{1/2} = 0.374$. The excellent agreement is somewhat fortuitous, for the plotted points show some scatter and the correct position of the line is accordingly uncertain. The main disadvantage of this procedure for obtaining rate constants is the need for an accurate p_∞ value.

General directions for making the least squares calculations for any functions are given by Deming.[4] For a reaction followed manometrically, volumetrically or dilatometrically, the reading error of p or v is independent of the magnitude of p or v. The correct least squares procedure is to minimize the sum of the squares of the residual $\Sigma(p_{\mathrm{obs}} - p_{\mathrm{calc}})^2$. This is most easily accomplished if p is obtained as an explicit function of time. Equations 7, 8 and 3 are the expression for half-order reactions, first-order reactions, and mixed half plus first-order reactions, respectively.

$$p = a + bt + ct^2 \qquad a = p_0,$$

$$b = (p_\infty - p_0)^{1/2}k_{1/2}, \qquad c = -(^1/_4)k_{1/2}^2 \qquad (7)$$

$$\text{or } k_{1/2} = (-4c)^{1/2},\ p_\infty = a - b^2/4c$$

$$p = a + be^{ct} \qquad a = p_\infty,$$

$$b = -(p_\infty - p_0), \qquad c = -k \qquad (8)$$

In carrying out the least squares adjustments, good approximations are obtained for the parameters. Then correction terms are computed for these initial values. For the two expressions involving exponentials the most convenient method of obtaining these initial estimates is to use one of the above-mentioned procedures for calculating the best possible estimate of the exponential constant c. Then using these "known" exponential terms for two corresponding p values one has two equations in two unknowns, a and b, and one can obtain good preliminary values for these parameters for eq. 8. For eq. 3 the corresponding procedure is to obtain

TABLE I

ILLUSTRATION OF TREATMENT OF DATA FOR A REACTION FOLLOWING MIXED HALF PLUS FIRST-ORDER KINETICS

Time, min.	Obsd. press. p, mm.	Smoothed press. p_s	$\mathrm{d}p/\mathrm{d}t$ (mm./min.)	$(p_\infty - p_s)^{1/2}$	$(\mathrm{d}p/\mathrm{d}t)$ $(p_\infty - p)^{1/2}$	p from eq.[c]
10	194.6	194.475	8.457	11.938	0.7084	
11	202.7	202.752	8.109	11.586	.6998	202.623
12	210.7	210.669	7.728	11.239	.6876	
13	218.2	218.227	7.375	10.898	.6767	218.273
14	225.3	225.461	7.103	10.561	.6725	
..	...	...	...	...	...	
27	293.5	293.487	3.579	6.596	.5426	293.313
28	296.9	296.961	3.557	6.328	.5304	
29	300.1	300.230				300.064
30	303.4	303.302				
31	306.1	306.147				306.025
39	323.1					323.077
41	325.9					325.885
43	328.1					328.203
45	330.1					330.054

[a] Preliminary equation: $p = 205.925 + 613.697\ e^{-0.0158t} - 734.931e^{-0.0316t}$. [b] Equation after first adjustment: $p = 174.124 + 718.185e^{-0.014761t} - 805.727e^{-0.029522t}$. [c] Equation after second adjustment: $p = 176.016 + 710.024 e^{-0.014913t} - 799.744e^{-0.029826t}$. Std. deviation of pressures = 0.106 with 14 D. F. over 202.7–330.1 mm. range. $k_1 = 0.0298$ with std. deviation 0.0008. $k_{1/2} = 0.374$ with std. deviation 0.030.

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(2) K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).

(3) E. Whittaker and G. Robinson, "The Calculus of Observation," 4th Ed., Blackie and Son Limited, London, 1944, p. 62, 315.

(4) W. E. Deming, "Statistical Adjustment of Data," John Wiley and Sons, Inc., New York, N. Y., 1943.

three equations in the three unknowns, *a*, *b* and *d*. It has been our practice to use ten points for eq. 7 and 8 (7 degrees of freedom) and eighteen to twenty points for eq. 3. The result of such an adjustment is given in the last column of Table I. The three equations at the foot of the table give an illustration of the rapidity of convergence. Usually a three parameter equation such as eq. 8 requires only a single adjustment if the original value for *c* is in error by no more than 10%.

Contribution from the Department of Chemistry
University of South Carolina
Columbia, South Carolina

The Thermal Decomposition of Nitrate Esters. III. *n*-Propyl Nitrate[1]

By Joseph B. Levy and Frank J. Adrian

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Previous papers in this series[2,3] have described a study of the thermal decomposition of ethyl nitrate using the infrared spectrometer as an analytical tool. The thermal decomposition of *n*-propyl nitrate has been examined in the same way and the results are reported here.

Experimental

The details of experimental procedure were the same as those used earlier.[2] *n*-Propyl nitrate was prepared from nitric acid and *n*-propyl alcohol. It was vacuum distilled at 150 mm. and a middle fraction taken. *n*-Propyl nitrite was prepared from nitrous acid and *n*-propanol, distilled and the fraction boiling at 56–58° used.

Results

The results obtained by the decomposition of samples of *n*-propyl nitrate at 191° for varying periods of time are shown in Table I. The initial pressures of *n*-propyl nitrate were of the order of 20 mm. Analyses for the *n*-propyl nitrate, *n*-propyl nitrite and nitroethane were made using the infrared absorption peaks at 11.68, 12.55 and 6.31 μ, respectively. Nitrogen dioxide and nitric oxide were analyzed colorimetrically as before.[2] The presence of formaldehyde in the products was indicated by its odor and by the deposition of a white deposit assumed to be paraformaldehyde[4] on the reaction bulb walls. No analyses were carried out for it however.

The effect of various additives on the rate of reaction and on the product distribution is shown in Table II.

Discussion

The above reaction products are analogous to those found for the ethyl nitrate decomposition and fit in well with the mechanism proposed.[2] The *n*-propyl nitrate case differs from the ethyl nitrate case in that (a) the nitro compound is a much more important product and (b) the kinetics obey a simple first-order law and are virtually unaffected by the addition of substantial amounts of nitric oxide (expts. 1, 6 and 7 of Table II). Both of these differences may be attributed to the fact that the *n*-propoxyl radical is less stable than the ethoxyl radical toward decomposition *via*

$$RCH_2O\cdot \longrightarrow R\cdot + CH_2O$$

This is in line with the general effect of structure on the stability of these radicals.[6]

Table I

The Thermal Decomposition of *n*-Propyl Nitrate at $181^{\circ b}$

Moles per mole of *n*-propyl nitrate initially present.

Time, min.	*n*-Propyl nitrate	*n*-Propyl nitrite	Nitroethane	Nitrogen dioxide	Nitric oxide	Total nitrogen	10^5k[a] sec.$^{-1}$
3.80	0.767	0.064	0.100	0.014	0.041	0.985	115
7.57	.581	.150	.164	.018	.059	0.973	119
10.55	.455	.249	.191	.040	.062	1.008	124
15.10	.371	.300	.263	.042	.070	1.048	110
22.57	.192	.380	.314	.042	.131	1.060	122
30.06	.122	.427	.324	.098	.103	1.078	117
50.10	.028	.455	.357	.014	.131	0.985	122
60.01	.005	.433	.404	.010	.149	1.000	
75.00	.005	.420	.400	.020	.275	1.120	

[b]$10^5k_{\text{av.}}$ = 118
Av. dev. = 4

[a] First-order rate constant. [b] From the data obtained manometrically by Phillips[5] the rate constant calculated at this temperature was 0.00093 sec.$^{-1}$

Table II

The Effect of Additives on the Thermal Decomposition of *n*-Propyl Nitrate at 181°

Expt.	Additive	Initial pressure (mm.)		Time, min.	Reaction, %	Yield,[a] %	
		C_3H_7-NO_3	Additive			C_3H_7-ONO	C_2H_5-NO_2
1	..	22.5	..	10.6	52.5	47.4	36.4
2	NO_2	22.0	18.1	30.0	54.0	84.0	23.4
3	O_2	22.2	32.0	30.1	33.3	23.0	52.6
4	O_2	18.5	70.2	60.7	39.4	20.5	42.5
6	NO	22.8	23.3	10.0	52.2	97.5	10.9
7	NO	22.5	50.1	10.0	55.0	100.0	4.8

[a] The fact that the yields exceed 100% for runs 2, 6 and 7 is attributed to the experimental error of the analysis.

The effects of the additives on the product distribution offer further support for the reaction mechanism.[2] The effect of added nitric oxide in boosting the yield of *n*-propyl nitrite at the expense of nitroethane is especially striking. The similar effect of nitrogen dioxide probably arises *via* its reduction to nitric oxide. The increase in the nitroethane yield at the expense of the *n*-propyl nitrite effected by the addition of oxygen may be explained by the oxidation of some of the nitrite ester back to the nitrate ester by the oxygen and the nitrogen dioxide formed in the decomposition. Ogg[7] has shown that ethyl nitrite is converted to ethyl nitrate by a mixture of nitrogen dioxide and oxygen although neither oxidant is effective alone.

The explanation of the effect of the additives on the kinetics follows that used for the ethyl nitrate case.[3]

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[1] Full experimental details of this work including infrared spectra can be found in the reference, J. B. Levy and F. J. Adrian, Navord, 2608, 1952.

[2] J. B. Levy, This Journal, **76**, 3254 (1954).

[3] J. B. Levy, *ibid.*, **76**, 3790 (1954).

[4] E. W. R. Steacie and G. T. Shaw, *Proc. Roy. Soc.* (*London*), **A146**, 388 (1934).

[5] L. Phillips, Thesis, University of London, 1949.

[6] F. F. Rust, F. H. Seubold, Jr., and W. E. Vaughan, This Journal, **72**, 338 (1950).

[7] R. A. Ogg, Jr., at "The Chemistry of the Oxides of Nitrogen," symposium sponsored by the Office of Ordnance Research, Chicago Illinois, September 3 and 4, 1953.