nitrogen that remained constant throughout the reaction. But since in some of the runs *p*-hydroxyazobenzene was formed, it is clear that some of the nitrogen deficit is due to coupling (eq. 3 and 4), a reaction that becomes increasingly important as

$$C_6H_5N_2^+ \xrightarrow{k_1} C_6H_5OH + N_2 + H^+ \qquad (3)$$

$$C_6H_5N_2^+ + C_6H_5OH \xrightarrow[k_2]{\text{buffer}} C_6H_5N_2C_6H_4OH + H^+ \qquad (4)$$

reaction proceeds. Thus the fraction of nitrogen evolved decreases throughout the reaction. Equations have been developed to allow for the coupling reaction,[4b] but these are not applicable to the last two runs in Table I because the extent of coupling exceeds that accommodated by the approximations used. The rate of the C–N cleavage step was therefore estimated by use of eq. 5 (*cf.* ref. 4b)

$$100(dp/dt)_0/a_0qv = \text{initial rate} \qquad (5)$$

in which a_0 is the initial diazonium salt concentration, q an apparatus constant, and v the solution volume in liters.[9] Since these initial rates are nearly independent of *p*H, the apparent acceleration in rate can largely be accounted for by the coupling reaction and is not evidence for a change of mechanism over to a homolytic one.

Acknowledgment.—The authors are indebted to the Rohm and Haas Company and to the U. S. Rubber Company for fellowships and to the Research Committee of the University of South Carolina for a grant for assistance in carrying out the extensive calculations involved.

Experimental

Rate Measurements.—The apparatus employed was the shaker equipment already described.[10] The reaction flask and the ballast flask each consisted of a 500-ml. 24/40 joint flask.

The diazonium salt was weighed out in a bucket constructed of Kel-F[11] with a platinum bail. These two materials seemed to be without effect on the reactions, although the point was not given a completely rigorous investigation. Glass buckets used initially caused rapid grinding of the flask interiors.

The oxygen-free reaction mixtures were prepared on a simple vacuum train consisting of vacuum feed, high purity nitrogen feed, reservoirs for distilled methanol, a sealed-on measuring tube and joints for attaching flasks. Spherical joints were less trouble than straight joints. The special head was a preliminary version of the type described before.[10] It consisted of a 24/40 inner joint with hook for the bucket to which was sealed a 2 mm. high-vacuum stopcock, on the other side of which was a joint for attaching the assembly to the vacuum train. To a side arm sealed to the flask side of the stopcock was attached a length of Tygon[12] tubing which was plugged when the flask was evacuated. The capillary tube and the second stopcock shown in Fig. 2 of ref. 10 were not used. Evacuation with the Tygon tubing in the system cannot be carried to less than about 10 μ. With the modified head (Fig. 2 of ref. 10) 0.01 μ is readily obtainable. In the reaction flask were placed acetic acid and sodium acetate, and the diazonium salt sample was placed in the basket. The assembly was attached to the vacuum train (side tube plugged), cooled with a Dry Ice bath, evacuated to 0.05 mm., then flushed with "high purity" grade tank nitrogen, the process being repeated twice more. Methanol was then distilled in from the measuring tube. The methanol had been outgassed by several trap to trap distillations. Nitrogen pressure was admitted to the loaded reaction flask, the flask disconnected from the train, allowed to warm almost to room temperature, then placed in the constant temperature bath. After an hour, the plug was removed from the Tygon line (the nitrogen pressure having been adjusted so that a little nitrogen escaped at this point) and the line was connected to the manometer.

Calculation of Initial Rates.—These were obtained from pressure *vs.* time graphs, from per cent. reaction *vs.* time graphs, and from log ($p_\infty - p$) *vs.* time graphs. The analytical method[9] did not work out as conveniently because of the S-shaped nature of the initial part of the curves. The initial rates in per cent. per second are based on the equation

$$\text{initial rate (\% per sec.)} = [100/(p_\infty - p_0)](dp/dt).$$

COLUMBIA, S. C.

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[10] D. F. DeTar, THIS JOURNAL, **78**, 3911 (1956).

[11] Trade Mark of the M. J. Kellogg Company for polychlorotrifluoroethylene.

[12] Polyvinyl chloride–polyvinyl acetate polymer.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY OF CORNELL UNIVERSITY AND FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

The Mechanisms of Diazonium Salt Reactions. V. A Kinetic Study of the Reactions of Benzenediazonium Fluoborate with Methanol in the Presence of Oxygen

BY DELOS F. DETAR[1] AND MELVIN N. TURETZKY[2]

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In methanol in the presence of oxygen and an acetate buffer the thermal decomposition of benzenediazonium salts is a complicated free radical reaction leading to dark brown reaction mixtures. Measurement of the initial rate under a variety of conditions has shown that the reaction is of mixed first plus half-order, and that the initial rate is approximately dependent on the square root of methoxide concentration and only slightly dependent on acetate ion concentration. Since there seems to be only one type of termination reaction which leads to a reaction of less than first order, namely, reaction of two phenyl radicals, the mechanism of the decomposition can be restricted to a small number of choices. The dependence on methoxide concentration rather than on acetate concentration indicates that the diazomethyl ether rather than the diazoacetate is the probable initiator.

In a continuation of work reported previously,[3] a preliminary study has been made of the kinetics of the reaction of benzenediazonium fluoborate with methanol in the presence of acetate buffers. The reaction is sufficiently complicated that even an extended investigation might not permit quantitative statements about its details. The present work, however, provides several indications about the reaction mechanism.

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[3] Part IV, D. F. DeTar and M. N. Turetzky, THIS JOURNAL, **78**, 3925 (1956).

TABLE I

THE THERMAL DECOMPOSITION OF BENZENEDIAZONIUM FLUOBORATE IN ANHYDROUS METHANOL IN THE PRESENCE OF ACETATE BUFFERS AND AIR AT 24.9 ± 0.1°

(50 ml. of solvent used unless otherwise noted.)

Run no.	Concn. ArN_2^+ $M \times 10^3$	Concn. NaOAc. $M \times 10^3$	log [NaOAc]/[HOAc][a] Initial	Final	Ionic strength	Apparent N_2 yield, %	$p_\infty - p_0$	Initial[b] rate mm./sec. × 100	Initial[c] rate, %/sec. × 100
141	20.0	188	−0.68	−0.74	0.26	49.4	251.0	5.68	1.118
120	20.0	188	− .68	− .74	.26	50.0	266.2	5.20	0.976
121	19.8	94	− .68	− .80	.27[e]	53.1	276.4	5.33	1.022
122	19.6	47	− .68	− .96	.27[f]	59.0	305.0	5.34	1.030
115	20.0	188	− .08	− .20	.26	41.9	222.7	9.06	1.70
114	19.5	94	− .08	− .25	.27[e]	44.1	220.7	7.69	1.53
131	19.9[d]	95	− .08	− .24	.27[e]	41.9	218.1	8.38	1.61
112	19.6	98	− .08	− .32	.15	40.4	212.4	9.94	1.89
116	19.8	56	− .08	− .38	.28[f]	46.3	245.6	7.58[g]	1.47
140	20.0	56	− .08	− .38	.28[f]	46.6	249.1	7.30	1.36
117	19.6	188	+ .52	+ .34	.27	38.6	197.6	20.6	4.02
118	19.8	94	+ .52	+ .19	.27[e]	38.5	204.0	15.6	2.94
119	19.6	56	+ .52	− .05	.28[f]	41.5	215.0	14.3	2.76
124	5.05[i]	96	− .08	− .11	.28[f]	42.1	296.8	12.9	1.82
130	45[d,h]	96	− .08	− .52	.28[f]	41.9	342.5	11.6	1.45
125	44.4[h]	96	− .08	− .52	.28[f]	52.3	416.5	11.4	1.43
113	36.6	97	− .08	− .40	.15	43.7	414.7	16.7	1.76
105	36.4	97	− .08	− .40	.15	47.3	456.7	19.4	2.00
128	28.6[d,h]	96	− .08	− .34	.28	41.2	219.1	7.44	1.43

[a] This is proportional to log $[CH_3O^-]$. [b] 100 dp/dt; p is mm. of p-xylene. Standard deviation is about 3.6 % relative. Calculated by Method 4. [c] Initial rate = $100(dp/dt)_0/a_0qv$ (eq. 7); a_0 = initial diazonium salt concn., molar; v = soln. vol. in liters; q = apparatus constant giving the mm. of xylene pressure corresponding to one mole of nitrogen. Std. dev. about 4% relative. [d] Benzenediazonium chloride. [e] LiCl 101 mmolar. [f] LiCl 141 mmolar. [g] Estimated from half-order reaction parameters based on $p_{\infty \text{obsd.}}$ [h] 35 ml. of methanol. [i] 200 ml. of methanol.

The investigation of the reactions of benzenediazonium salts in methanol began with a product study of the brown reaction mixtures obtained in the presence of air.[4,5] This was followed by a series of preliminary rate experiments which led to the significant discovery of the effect of oxygen on the reaction rate. These preliminary runs are not quantitatively significant because they were swept with nitrogen in such a fashion that the amount of oxygen remaining was a significant and unknown variable. After discovery of the oxygen effect, the experiments were planned anew. Rate studies carried out on air-saturated reaction mixtures are reported in this paper. Rate studies[3] and product studies[4] in the absence of oxygen are reported elsewhere.

Attempts were made to correlate the rate data within the runs by means of various standard rate expressions. The half-order expression (eq. 3) worked out moderately well, but the data are perhaps somewhat better correlated by the equation for a reaction of first plus half-order (eq. 6).[6]

For a reaction of half order

$$-d[ArN_2^+]/dt = k_{1/2}[ArN_2^+]^{1/2} \qquad (1)$$

$$dp/dt = k_{1/2}'(p_\infty - p)^{1/2} \qquad (2)$$

$$p = a + bt + ct^2 \qquad (3)$$

Equation 3 is the integrated form of eq. 2; $k_{1/2}' = (-4c)^{1/2}$ and $k_{1/2} = k_{1/2}'(qv)^{-1/2}$. In these equations v is soln. vol. in l., q is the apparatus constant defined by the expression $(p - p_0) = (a_0 - x)qv$ with a_0 the initial diazonium salt concn. (moles/l.), and x the concn. at time t.

For a reaction of first plus half-order

$$-d[ArN_2^+]/dt = k_1[ArN_2^+] + k_{1/2}[[ArN_2^+]^{1/2} \qquad (4)$$

$$dp/dt = k'(p_\infty - p) + k_{1/2}'(p \quad - p)^{1/2} \qquad (5)$$

$$p = a + be^{ct} + de^{2ct} \qquad (6)$$

$$100(dp/dt)_0/a_0qv = 100k_1 + 100k_{1/2}a_0^{-1/2} \qquad (7)$$

Equation 6 is the integrated form of eq. 5 with $k'_1 = -2c$ and $k'_{1/2} = -cb/(-d)^{1/2}$; $k_1 = k_1'$ and $k_{1/2} = k'_{1/2}(qv)^{-1/2}$. The term on the left of eq. 7 is the initial rate in per cent. per sec. The units of k_1 are sec.$^{-1}$ and of $k_{1/2}$ are mole$^{1/2}$ l.$^{-1/2}$ sec.$^{-1}$.

The correlations obtained with eq. 3 and 6 were not as satisfactory as those reported previously for other reactions.[7,8] As explained later it is quite possible that the correct rate expression is still more complex. For this reason the initial rates perhaps afford a more valid basis for comparison than do constants obtained somewhat arbitrarily by eq. 3 or 6. Initial rates were calculated by several methods as described in the Experimental section. These rates appear to have a standard deviation of about 4% based on a variance analysis. A summary of the experimental data is given in Table I.

In writing eqs. 1–7 the assumption is made that the nitrogen yield is quantitative in order that $p_\infty - p_0 = a_0qv$ (8). This assumption is not true for experiments summarized in Table I. The low apparent nitrogen yields can be ascribed to two processes: a process which gives nitrogen-containing products and a process which involves oxygen absorption. Attempts to analyze the reaction products more completely than already reported[4] have not been fruitful, but the amount of nitrogen present in the products does not seem large. There are two prac-

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[4] D. F. DeTar and M. N. Turetzky, THIS JOURNAL, **77**, 1745 (1955).

[5] D. F. DeTar, *ibid.*, **73**, 1446 (1951).

[6] D. F. DeTar, *ibid.*, **77**, 2013 (1955).

[7] D. F. DeTar and A. R. Ballentine, *ibid.*, **78**, 3916 (1956).

[8] D. F. DeTar and S. Kwong, *ibid.*, **78**, 3921 (1956).

tical alternatives in treating the data: the initial rate as defined by the left side of eq. 7 can be used or else this initial rate can be divided by the fractional apparent nitrogen yield. The first alternative is valid if initially the nitrogen yield is quantitative or if in all runs considered the initial apparent nitrogen yield is a constant fraction of the diazonium salt decomposed. The second alternative is valid if the apparent fractional nitrogen yield is constant throughout the reactions. The first alternative has been arbitrarily selected since the second one leads to no useful relationships.

The dependence of the initial rate on the diazonium salt concentration was investigated for a series of six runs carried out at a constant acetate level, a constant buffer ratio, and a constant ionic strength using a ninefold variation in diazonium salt concentration (runs 131, 128, 130, 124, 114 and 125). The results can be expressed as: initial rate (% sec.) = 0.0118 + 5.01 × 10^{-4} (concn. ArN_2^+ mole/l.)$^{1/2}$ with a standard deviation in initial rates of 4% relative. Thus the first plus half-order expression (eq. 7) correlates the data adequately. Since three of the runs were carried out with the chloride and three with the fluoborate, it can be concluded that neither of these ions exerts a special effect.

The value of the first-order rate constant, 1.18 × 10^{-4} sec.$^{-1}$, may be compared with the value 0.97 × 10^{-4} sec.$^{-1}$ obtained for the ionic reaction,[3] and with the values 1.07 × 10^{-4} and 0.94 × 10^{-4} sec.$^{-1}$ from the half-plus first-order equations for runs 131 and 114, respectively. The value of $k_{1/2}$ = 5.0 × 10^{-3} mole$^{1/2}$ l.$^{-1/2}$ sec.$^{-1}$ is however smaller than the values obtained from the half plus first-order expressions for runs 131 and 114; these were 26 × 10^{-6} and 20 × 10^{-6}, respectively, based on $k'_{1/2}$ in terms of pressures and assuming a quantitative nitrogen yield. According to the initial rate expression above approximately 25% of the initial reaction is accounted for by the half-order term, but according to the first plus half-order expression about 70% of the initial reaction is due to the half-order term. The difference arises from the occurrence of the oxygen absorption reaction.

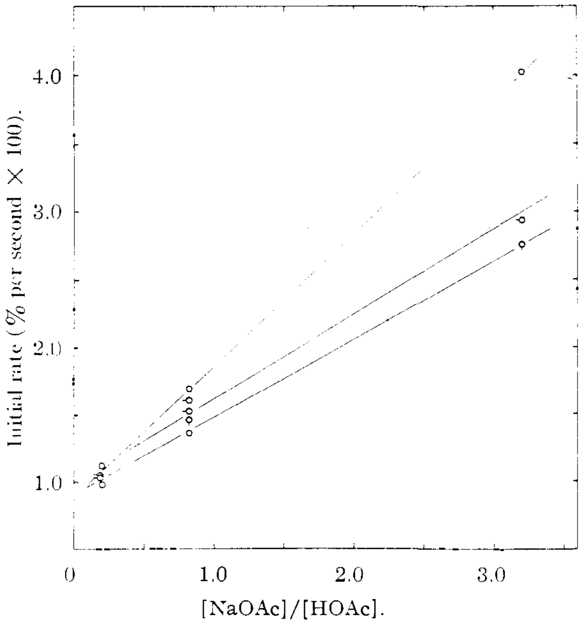

Fig. 1.—Initial rate of nitrogen evolution from benzenediazonium fluoborate in methanol in the presence of air as a function of the acetate/acetic acid ratio at various acetate ion levels. Acetate concentration 0.188 *M* ○; 0.094 *M* -○; 0.056 *M* ♀.

The variation of the initial reaction rate with buffer composition is shown in Fig. 1. The initial rate is plotted against the ratio of acetate ion to acetic acid for various initial sodium acetate levels. The ionic strength was maintained constant at 0.26 by use of lithium chloride. The buffer ratio is proportional to the methoxide ion concentration. The lower two lines have a slope of about one half, and the upper line has a slope of about unity. At the lower values of the buffer ratio the rate is nearly independent of acetate ion concentration. Run 117 constitutes the only discordant point, but run 117 with 3.4 times as much acetate as run 119 is only 1.5 times as fast, and this is an exponential dependence of considerably less than one-half.

Discussion

A series of eight reaction steps has been proposed to account for the products of and for the kinetics of the thermal decomposition of benzenediazonium salts in methanol in the presence of an acetate buffer and in the absence of oxygen. In the presence of oxygen a number of additional steps require consideration. These are to be considered as a continuation of the equations previously given.[4]

$$C_6H_5\cdot + O_2 \dashrightarrow C_6H_5OO\cdot \qquad (9)$$

$$HOCH_2\cdot + O_2 \dashrightarrow HOCH_2OO\cdot \qquad (10)$$

$$C_6H_5OO\cdot {}^+CH_3OH \dashrightarrow C_6H_5OOH + \cdot CH_2OH \qquad (11)$$

$$HOCH_2OO\cdot + CH_3OH \dashrightarrow HOCH_2OOH + \cdot CH_2OH \qquad (12)$$

$$HOCH_2OO\cdot + C_6H_5N_2^- \dashrightarrow HCOOOH + N_2 + H^+ + C_6H_5\cdot \qquad (13)$$

$$C_6H_5\cdot + C_6H_5OO\cdot \longrightarrow \text{products} \qquad (14)$$

$$C_6H_5\cdot + HOCH_2OO\cdot \dashrightarrow \text{products} \qquad (15)$$

$$C_6H_5OO\cdot + \cdot CH_2OH \dashrightarrow \text{products} \qquad (16)$$

$$HOCH_2OO\cdot + \cdot CH_2OH \dashrightarrow \text{products} \qquad (17)$$

$$2C_6H_5OO\cdot \dashrightarrow \text{products} \qquad (18)$$

$$2HOCH_2COO\cdot \dashrightarrow \text{products} \qquad (19)$$

$$C_6H_5OO\cdot + HOCH_2OO\cdot \dashrightarrow \text{products} \qquad (20)$$

$$2\cdot CH_2OH \longrightarrow \text{products} \qquad (21)$$

More than thirty different mechanisms involving all ten of the possible termination steps were examined to determine the order of dependence upon the diazonium salt concentration. It was relatively simpler to do this for the rate of disappearance of diazonium salt than for the more complicated actual case involving measurement of the difference between the nitrogen evolution rate and the oxygen absorption rate, though in many cases the order was the same for both differentials. One simplifying principle exists: if the nitrogen evolution and the oxygen absorption are of the same order, then the over-all reaction is of that order.

However, many of the resulting expressions are complicated. For example, a mechanism involving steps 1–5, 10, 12 and 6 as far as gas evolution is concerned contains terms with the diazonium salt concentration to the first, the one-half, and the minus one-half powers.

Only one type of termination leads to an order less than first: termination by reaction 6 (two phenyl radicals reacting); such a termination usually gives a reaction of first plus half-order. Examples are mechanisms consisting of reactions 1–5, 9, 11, 6 and 1–5, 10, 13, 6 and 1–5, 9–12, 6 in addition to the mechanism 1–5, 10, 12, 6 cited above. All of the other nine termination steps lead to terms of at least first order and on up to second order.

While it is not possible to be sure that some other complicated function will not lead to an expression which gives a fair fit to a half-order or a first-plus half-order expression, it is encouraging that a chemically reasonable mechanism does account for the results in a satisfactory fashion.

TABLE II

EVALUATION OF THE INITIAL RATE OBTAINED BY VARIOUS METHODS

(Tabulated values are per cent. per second × 100)

Run no.	$p - t$ Method 1	Half-order Method 2	First + half Method 3	Anal. Method 4
140	2.85	3.13	2.92	2.98
131	3.42	3.93	3.80	3.73
116	2.63	3.02	3.13	3.35
114	3.22	3.62	3.30	3.48
112	4.28	4.53	4.67	4.66

The effect of buffers enters into the rate expression *via* equation 1a or 1b. If the diazomethyl ether is the effective initiator, then the rate should depend on the square root of the acetate to acetic acid ratio. If the diazoacetate is the initiator, then the rate should depend instead on the half power of the acetate ion concentration. The results cited above (Fig. 1) suggest that the diazo ether is considerably more important than the diazoacetate.

Acknowledgment.—The authors are pleased to acknowledge the help of the Rohm and Haas Company and of the U. S. Rubber Company by providing fellowships and of the University of South Carolina Research Committee for a grant for assistance with the calculations.

Experimental

Apparatus and Procedure.—The apparatus employed the shaker assembly already described.[9] Crystalline benzenediazonium fluoborate and benzenediazonium chloride were prepared. Reagent grade methanol was used without further purification. Since the kinetic results obtained had a fairly large standard deviation the corrections for the p^2 term were not applied. The order in which the runs were carried out is given by the run no. (which are notebook page numbers).

Evaluation of the Half-order Rate Expression.—The observed pressure values within the individual runs could be approximated fairly well using the half-order expression $p = a + bt + ct^2$, the average standard deviations for fourteen runs was 0.45 mm. and the average range of reaction over which the equation was valid was 15–87%.

Evaluation of the First Plus Half-order Rate Expression.—Since the ionic decomposition of the diazonium salt to anisole is a parallel first-order reaction competing with the half-order free radical chain reaction in the present runs, the reactions should more accurately be represented by the expression for a reaction of first plus half-order than by the half-order expression. While the rate of the ionic reaction sets a minimum on the value of the first-order constant, the value could be much greater if part of the free radical decomposition were also of first order. The appropriate expression is $p = a + be^{ct} + de^{2ct}$. Since it is a tedious job to carry out complete least squares adjustments with this expression, especially when the first-order component is much less important than the half-order component, such adjustments have not been carried out in full. Partially adjusted sets of parameters were obtained for five runs, and it was found that the first plus half-order expression fitted the data at least as well as, and in some runs better than, the half-order expression.

Determination of Initial Rates.—The initial rate of the reaction in per cent. per second is given by eq. 7. The particular difficulty in estimating initial rates is due to the experimental fact that temperature equilibria and saturation equilibria are at their very worst in the initial stages of the reaction. The value of p_0 obtained with even the best behaved of first-order reactions and with the most refined techniques is often a few mm. different from the p_0 value required by the kinetic expression which accounts accurately for the reaction from 10 to 98% reaction. Four methods were used to evaluate the initial rate: (1) An initial slope was obtained from a large scale p–t curve. (2) The slope was obtained by differentiating the half-order expression. (3) The slope was obtained by differentiating the first plus half-order expression. (4) An analytical estimate was made of dp/dt as described below. The results for five runs are presented in Table II. The entries were converted to their natural logarithm and a variance analysis carried out. The variability due to rows (runs) and that due to columns (methods) were eliminated (both were significant at much less than the 1% level); the standard deviation estimated from the residual variance was 3.6% rela-

TABLE III

ILLUSTRATION OF ANALYTICAL COMPUTATION OF INITIAL RATE FOR RUN 114

$$\log (\mathrm{d}p/\mathrm{d}t) = -0.3087 + 0.4150 \log(p_\infty - p)$$

t (min.)	p	$\Delta^1 p$	$\Delta^2 p$	4 dp/dt	dp/dt	log ($p_\infty - p$)	log (dp/dt)	F_0[a]
4	68.9	17.5	−1.4	18.2	4.55	2.3094	0.6580	0.0084
8	86.4	16.1	+0.7	15.8	3.95	2.2605	.5966	− .0327
12	102.5	16.8	−1.4	17.5	4.38	2.2312	.6415	+ .0243
16	119.3	15.4	−1.2	16.0	4.00	2.1861	.6021	.0037
20	134.7	14.2	+0.4	14.0	3.50	2.1302	.5441	− .0311
24	148.9	14.6	−1.3	15.3	3.83	2.0831	.5832	+ .0275
28	163.5	13.3						
32	176.8							
0	52.1					2.3438	(.6639)[b]	
∞	272.8							

[a] Obsd. value of log(dp/dt) − calcd. value. The discrepancies are rather larger than usual but run 114 was chosen as the example since other data for this run are given in Table II. [b] Calculated from the equation. The initial rate in per cent. per minute, R_i, is given by the expression $\log R_i = 2 + 0.6639 - 2.3438$, and the standard deviation even with the rather large F_0 values is still fairly small, 5% relative.

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[9] D. F. DeTar, THIS JOURNAL, **78**, 3911 (1956).

tive with 12 D.F. The initial rates estimated from the p–t values (method 1) were significantly low (by about 8%), but the values estimated by the other three methods were the same within the experimental error. Because of simplicity of computation and for the sake of uniformity, the initial rates discussed in this paper are all based on method 4, the analytical method described below.

Analytical Method for Determining Initial Rates.—An approximate equation for the rate of a reaction is given by the expression $dp/dt = k(p_\infty - p)^b$. This expression allows two parameters, a rate constant k and a reaction order b. The logarithmic expression is $\log (dp/dt) = \log k + b \log (p_\infty - p)$, from which b and $\log k$ are the slope and intercept of the linear relationship. The initial value of dp/dt is obtained by substituting the value $(p_\infty - p_0)$. The problem of obtaining suitable values of dp/dt was easy to solve. Since $dp/dt = (1/\Delta t)[\Delta^1 p - (^1/_2)\Delta^2 p + \ldots]$,[10] a table was prepared giving p as a function of t at even time intervals Δt. (The data had been taken at even time intervals in order to facilitate such computations.) From the appropriate column of first differences of p $(\Delta^1 p)$ and of second differences of p $(\Delta^2 p)$ it was possible to calculate values of dp/dt corresponding to several values of $(p_\infty - p)$. Parameters for a suitable straight line were obtained by the averaging method in which the points were divided into two equal groups. The calculation is illustrated in Table III. The range of values used was from about 5–50% of reaction. This analytical calculation is much faster than a graphical procedure of comparable accuracy.

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[10] E. Whittaker and G. Robinson, "The Calculus of Observation," 4th Ed., Blackie and Son Limited, London, 1944.

COLUMBIA, S. C.

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

The Inductive Effect and Chemical Reactivity. IV. Dipole Moments of Halogen Derivatives of Aliphatic Hydrocarbons[1]

BY RICHARD P. SMITH AND EARL M. MORTENSEN

RECEIVED JANUARY 30, 1956

Electric dipole moments are calculated for halogen substituted aliphatic hydrocarbons (except in cases where the moment is dependent upon internal rotation) by the theory of Smith, Ree, Magee and Eyring. The polarizability parameter for the C–C bond is changed; all other parameters retain their original values. Excellent agreement with observed moments is obtained in almost every case. The relationship of this theory to other theories for correlating dipole moment and structure is discussed.

Introduction

A simple model for the calculation of inductive charge shifts in organic molecules was proposed in the first paper of this series[2] (hereafter referred to as Part I) and dipole moments were calculated for halogen-substituted methanes and for ethyl halides. The application of the method to molecules containing carbon–carbon bonds was discussed and illustrated in a subsequent paper[3] (part II).

The calculated moments for halogen-substituted methanes obtained in Part I were in good agreement with experiment. In addition it was successfully predicted that, while a decreased moment results in going from CH_3X to CH_2X_2 for X = Cl, Br or I, an increased moment should result in going from CH_3F to CH_2F_2. For in part I, methylene fluoride was predicted to have a moment of 1.91 *D;* an experimental value of 1.96 ± 0.02 *D* was subsequently observed by Lide,[4] this being appreciably higher than the moment of methyl fluoride.

However, the good agreement obtained in the Part I calculation of substituted-methane moments did not extend to the ethyl halides. It was suggested that these results did not warrant calculation of dipole moments of higher aliphatic derivatives, where the dipole moments would be even more sensitive to the charge distributions. It was pointed out that calculated charge shifts, on the other hand, were relatively insensitive to the parameters used. Hence the justification for discussing relative rates in terms of charge shifts, as was done in the second and third[5] papers of this series.

We now find that it is indeed possible to calculate moments of most halogen-substituted saturated hydrocarbons in good agreement with experiment. It is only necessary to revise the value of one parameter, the longitudinal polarizability of the carbon–carbon bond. This revision is independently demanded by the polarizability data.

In this paper, our considerations will be limited to halogenated saturated hydrocarbons having moments which are not dependent upon configuration, *i.e.*, molecules where potential barriers hindering rotation need not be considered in a discussion of dipole moments. In addition to presenting the numerical calculations, it will be pointed out that a number of trends in the moments of higher aliphatic halides are satisfactorily accounted for, though they have previously caused difficulty. For example, isopropylidene chloride has a higher moment than does isopropyl chloride, while methylene chloride has a lower moment than methyl chloride.[6] Our charge-shift model of Part I gives satisfactory qualitative and quantitative interpretations of such trends.

Calculations

The generally-high values found for moments of ethyl halides in Part I seem to indicate that the calculations allow too much C–C bond polarization, *i.e.*, $\beta_C{}^C$ (notation of Part I) is too high. According to Part I

$$\beta_C{}^C = \frac{S_C(b_1)^{C-C}}{R_{CC}R_C{}^2} \qquad (1)$$

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