These correspond to the mechanism assumed in deriving equation 2

$$\mathrm{ROCS_2^-} + \mathrm{H^+} \longrightarrow \mathrm{X}^{\ddagger} \longrightarrow \text{products} \qquad (4)$$

According to the Christiansen–Scatchard equation, written without the Brønsted salt effect term

$$\log k = \log k_\infty - \frac{Z_A Z_B \epsilon^2}{2.3kTDr} \qquad (5)$$

log k should be a linear function of $1/D$ at each temperature.[5] If kK_0 were truly independent of the dielectric constant D, log K_0 should be linear with $1/D$ with slope of opposite sign; this is not true even over the range considered here.

Since K_0 and D are known much more precisely than kK_0 from the rate measurements, equation 3 must be taken as an approximation, and in calculating activation energies for process (4), or rate constants freed from electrostatic effects, the experimental data should be used rather than equation 3.

We have calculated log k, obtaining log K_0 from the equations of Harned and Fallon.[6] Extrapolation to 60° is required and the following equation was used

$$\log K_0 = -4.82 - 11.59N \text{ at } 60° \qquad (6)$$

where N is the mole fraction dioxane. The dielectric constant D is easily interpolated from the data of Åkerlöf and Short.[7] From plots of log k *vs.* $1/D$, equation 5, which are linear within experimental error, the critical complex radius r was determined to be 1.72 ± 0.07 Å., a value near that found for ethyl xanthate.[4]

Table II gives activation energies E_{expt} and the Arrhenius log A from the least squares equations for log k *vs.* $1/T$. Since $E_{\text{expt}} = \Delta H^* + RT = \Delta E^* + RT$, the "absolute rate" equation becomes

$$k = 60e\frac{kT}{h}\exp\left(-\frac{E_{\text{expt}}}{RT}\right)\exp\left(-\frac{\Delta S^*}{R}\right) \qquad (7)$$

(where 60 enters because k is in liter mole^{-1} min.$^{-1}$). The contribution of D to E_{expt} and ΔS^* can be calculated from equations given in the references cited,[5] and consequently E_∞ and ΔS^*_∞ values freed from electrostatic effects can be calculated. These are included in Table II.

TABLE II

ENERGY AND ENTROPY OF ACTIVATION

Dioxane, wt. %	log A	E_{expt}, cal./mole	E_∞, cal./mole	ΔS^*, 303°K.	ΔS^*_∞, 303°K.
0	15.09	17250	16200	0.37	−11.37
10.2	15.20	17100	15750	0.87	−12.91
20.2	15.57	17100	14850	2.56	−13.97
30.1	16.67	18150	15800	7.58	−12.78

The values of E_∞ and ΔS^*_∞ should be constant independently of the solution from which the calculation is made. While E_∞ is no more constant than E_{expt}, ΔS^*_∞ is satisfactory. The values are somewhat larger numerically than was found for ethyl xanthate.

Comparison with collision theory may be made through the equation

$$\log PZ_0 = \log 60e\frac{kT}{h} + \frac{\Delta S^*_\infty}{2.3R} \qquad (8)$$

At 303°K., the right side = 15.01 − 2.79 = 12.22. Now

$$Z_0 = \frac{60N}{1000}\sigma^2\left[\frac{8\pi RT}{\mu}\right]^{1/2} \qquad (9)$$

Using σ = 1.72 Å. and $\mu = (135 \times 19)/154 = 16.66$

$$\log Z_0 = 12.37$$

As is usual for this type of reaction, there is no great discrepancy.

NEW YORK, N. Y.

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[5] This and other equations used may be found in (a) E. S. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Co., New York, 1949; (b) J. C. Warner, *Ann. N. Y. Acad. Sci.*, **39**, 345 (1940).

[6] H. S. Harned and L. D. Fallon, THIS JOURNAL, **61**, 2377 (1939).

[7] G. Åkerlöf and O. A. Short, *ibid.*, **58**, 1241 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE A. AND M. COLLEGE OF TEXAS]

Rates of Reaction of Diphenyldiazomethane with Aliphatic Carboxylic Acids in Toluene[1]

BY A. BERNARD HOEFELMEYER AND C. KINNEY HANCOCK

RECEIVED APRIL 26, 1955

Rate constants at 25° have been determined for the reaction of diphenyldiazomethane with 28 carboxylic acids in toluene. Statistical treatment of fifteen log k_2 values for which Taft's σ^*-values are available yields the following results: (1) equation of the regression line, log $k_2 = -0.603 + 2.80\ \sigma^*$, where 2.80 is the reaction constant ρ^*; (2) standard deviation from the regression line, 0.0941; (3) correlation coefficient, 0.998. Use of the equation, $\sigma^* = 0.215 + 0.356 \log k_2$, yields hitherto unreported σ^*-values for 11 substituents. The anomalous cases of formic and benzoic acids are discussed. The relatively large ρ^*-value of 2.80 may be of value in determining small differences in polarity.

Introduction

Taft[2] has proposed an equation, $\log k/k_0 = \sigma^*\rho^*$, for correlating polar substituent constants with rate or equilibrium constants for aliphatic reaction series having essentially constant steric and resonance factors. This equation is quite similar to that of Hammett,[3] $\log k - \log k^0 = \rho\sigma$, which has been applied so widely to reactions of *m*- and *p*-substituted benzene derivatives.

The present study was undertaken in order to determine if the Taft equation is applicable to the rates of reaction of diphenyldiazomethane (DDM) in toluene at 25° with carboxylic acids. This research was carried out independently of, but more or less parallel to, that of Taft and Smith[4] who studied the reactions of DDM in ethanol at 25° with 13 carboxylic acids, seven of which were included in the present study.

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[1] Abstracted from the Ph.D. dissertation of A. B. Hoefelmeyer, The A. and M. College of Texas, 1954. Celanese Corporation of America, Clarkwood, Texas.

[2] R. W. Taft, Jr., THIS JOURNAL, **75**, 4231 (1953).

[3] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 186.

[4] R. W. Taft, Jr., and D. J. Smith, THIS JOURNAL, **76**, 305 (1954).

Experimental

Materials.—DDM was prepared[5] from benzophenone hydrazone.[6] Recrystallization from methanol gave fluffy red crystals, m.p. 30.5–31.0°. Assays of about 97% DDM were obtained by treating toluene solutions of DDM with excess benzoic acid and back-titrating with sodium hydroxide solution. At 550 mμ, the impurities had no effect on the optical density (OD) of DDM in toluene since the OD of the DDM-excess benzoic acid reaction product was the same as the OD of toluene.

α-Methylbutyric, pivalic and caproic acids were prepared by well-known methods. Other materials were procured from commercial sources. In some cases, purification was necessary in order to obtain physical constants in good agreement with literature values.

Rate Measurements.—The procedure was similar to that of Roberts, *et al.*[7] A Beckman model B spectrophotometer was used to follow (at 550 mμ) the reactions. The temperature of the laboratory was maintained at 24.8 ± 0.2°.

At 25.00 ± 0.01°, 50 ml. of 0.0600 *M* acid and 50 ml. of approximate 0.00600 *M* DDM were mixed and allowed to react at the same temperature. At convenient time intervals, samples of reaction mixture were transferred to the spectrophotometer cell, the OD measured, and the sample discarded. This required about 40 seconds during which no appreciable temperature change was noted. Except for pivalic acid, which reacted most slowly, all reactions were followed for at least two half-lives of DDM decomposition.

For acids having a DDM decomposition half-life of less than five minutes, it was necessary to modify the procedure by retaining in the spectrophotometer cell the first sample of reaction mixture transferred from the 25.00° bath and following the reaction in this sample. No appreciable temperature change of the reaction mixture was observed during the short reaction period. This method proved satisfactory even for chloroacetic acid which had a half-life of less than 10 seconds.

Four to six rate determinations were made on each acid. The second-order rate constants were obtained by dividing the pseudo first-order rate constants by the acid concentration. The maximum deviation from the mean of replicate k_2 values exceeded 5% in only the cases of the following five acids: formic, 9%; β-bromopropionic, 11%; β-chloropropionic, 6%; methoxyacetic, 7%; phenoxyacetic, 6%.

Results and Discussion

Average k_2 values are given in Table I. Available σ^*-values by Taft[2] are shown in the first seventeen lines of Table I and are plotted against corresponding log k_2 values in Fig. 1. Excluding values for formic and benzoic acids, statistical treatment[8] of the data for the other fifteen acids yields the following results: (1) equation of the regression line, log $k_2 = -0.603 + 2.80\ \sigma^*$, where 2.80 is the reaction constant ρ^*; (2) standard deviation from the regression line, 0.0941; correlation coefficient, 0.998. The regression line is shown in Fig. 1. The ρ^*-value of 2.80 corresponds to minimizing the squares of the deviations along the log k_2-axis. By minimizing the squares of the deviations along the σ^*-axis, the equation, $\sigma^* = 0.215 + 0.356 \log k_2$, was obtained and used to calculate the σ^*-values for the other acids which are given in the last eleven lines of Table I.

The exclusion from the statistical treatment of the data for formic and acetic acids is justified since these two acids are not substituted acetic acids while the other twenty-six acids are. Also, because of the peculiar properties of formic acid and the aromatic character of benzoic acid, it could hardly be expected that rate data for these two acids would correlate satisfactorily with rate data for the twenty-six substituted acetic acids.

TABLE I

RATE AND SUBSTITUENT CONSTANTS FOR REACTIONS OF DIPHENYLDIAZOMETHANE WITH CARBOXYLIC ACIDS, RCOOH, IN TOLUENE AT 25°

No.	Subst., R	k_2, l. mole^{-1} min.$^{-1}$	σ^*
1	H	32.1	+0.490[a]
2	CH_3	0.204	.000[a]
3	C_2H_5	.107	− .100[a]
4	*n*-C_3H_7	.100	− .115[a]
5	*i*-C_3H_7	.0730	− .200[a]
6	*n*-C_4H_9	.0873	− .130[a]
7	*i*-C_4H_9	.0911	− .125[a]
8	*s*-C_4H_9	.0720	− .210[a]
9	*t*-C_4H_9	.0408	− .320[a]
12	$(C_2H_5)_2CH$	.0739	− .225[a]
17	$ClCH_2$	201	+1.050[a]
18	$BrCH_2$	170	+1.030[a]
23	$ClCH_2CH_2$	4.92	+0.385[a]
24	CH_3OCH_2	7.39	+ .520[a]
26	$C_6H_5OCH_2$	65.7	+ .850[a]
27	$C_6H_5CH_2$	0.973	+ .225[a]
28	C_6H_5	.642	+ .600[a]
10	*n*-C_5H_{11}	.0870	− .162[b]
11	*i*-C_5H_{11}	.0873	− .162[b]
13	*n*-C_6H_{13}	.0858	− .165[b]
14	*n*-C_7H_{15}	.0852	− .166[b]
15	*n*-C_8H_{17}	.0952	− .148[b]
16	*n*-C_9H_{19}	.0929	− .152[b]
19	ICH_2	68.2	+ .868[b]
20	CH_3CHBr	86.1	+ .903[b]
21	CH_3CHCl	112	+ .944[b]
22	$BrCH_2CH_2$	5.73	+ .485[b]
25	$C_2H_5OCH_2$	6.10	+ .495[b]

[a] Values of Taft.[2] [b] Values calculated from $\sigma^* = 0.215 + 0.356 \log k_2$.

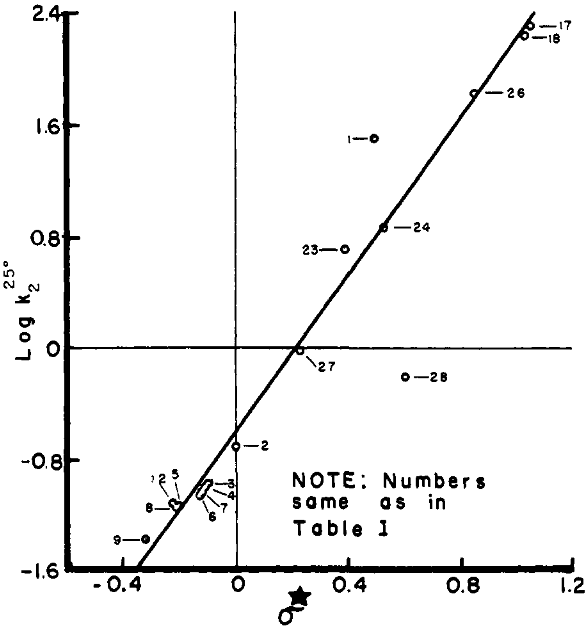

Fig. 1.—Correlation between the second-order rate constants for the reaction of diphenyldiazomethane with carboxylic acids in toluene at 25° and Taft's polar substituent constants.

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(5) *Org. Syntheses*, **24**, 53 (1944).

(6) H. H. Szmant and C. McGinnis, THIS JOURNAL, **72**, 2890 (1950).

(7) J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2923 (1949).

(8) H. H. Jaffé, *Chem. Revs.*, **53**, 253 (1953).

Taft and Smith[4] determined the rates of reaction of DDM in ethanol at 25° with thirteen carboxylic acids and found a ρ^* value of 1.175 ± 0.043. The relatively larger ρ^* value of 2.80 found in the present study for the reaction in toluene at 25° may be helpful in determining more accurately small differences in polarity.

COLLEGE STATION, TEXAS

[CONTRIBUTION FROM THE ALLEGANY BALLISTICS LABORATORY,[1] HERCULES POWDER COMPANY]

Burning Rates of Deuterated Nitrate Esters

BY RUDOLPH STEINBERGER, CHARLES A. ORLICK AND VINCENT P. SCHAAF

RECEIVED MARCH 28, 1955

Several deuterated nitrate esters have been prepared and their burning rates measured. The results are in agreement with the hypothesis that the diffusion of atomic hydrogen is an important mechanism of energy feedback in these flames and that the principal initial reaction involves attack by atomic hydrogen on nitrate ester.

Previous work on temperature profiles of burning liquid nitrate esters[2] has shown that the temperature and the temperature gradients at the liquid–gas interface are very low. In view of the somewhat different interpretation of quite similar data by others[3] it must be recognized that this experimental result cannot be accepted at present without some reservation. Nevertheless, considerable doubt has been thrown on a widely accepted mechanism of propagation of the combustion front. According to this mechanism,[4] heat is transmitted from the hot combustion gases to the surface of the condensed phase by conduction and radiation, and heat is also generated in the top layer of the condensed phase by exothermic decomposition reactions. The resulting high temperature in the surface layer is supposed to lead to gasification by decomposition or volatilization.

Our evidence indicated that the surface temperatures were too low to account for the observed rate of burning on the basis of the thermal mechanism. Therefore it was decided to examine another mechanism. involving attack by free radicals on the nitrate ester. Such a scheme emphasizes the role of diffusion of matter rather than of heat as a method of energy transport in flame propagation, inasmuch as the free radicals must be formed in the hot part of the flame and must diffuse back through the intermediate gases to the liquid surface. This type of mechanism has received considerable attention in the field of gaseous flames.[5] To our knowledge it has not been considered seriously in previous work on solid or liquid fuels.

Of the possible free radicals which might attack the nitrate ester the one which diffuses most readily and therefore is the most likely active species is atomic hydrogen. The substitution of deuterium for hydrogen should thus have a pronounced retarding effect on the burning rate. In order to test this scheme, several deuterated nitrate esters have been prepared and their burning rates measured. The results are in qualitative agreement with expectations based on the free radical hypothesis.

Experimental

Materials.—The deuterated starting materials were obtained at an isotopic purity of 95% or better from a commercial supplier.[6] The preparations followed the general course: alcohol → halide → nitrate and were found to proceed without appreciable exchange.

Ethyl Nitrate-d_5.—A mixture of 0.5 g. (16 meq.) of red phosphorus, 1.66 g. (31.9 mmoles) of ethyl alcohol-d_6, and 4.3 g. (33.9 meq.) of resublimed iodine was refluxed for 2.5 hr. The deuterated ethyl iodide produced in this reaction was distilled into a cooled flask containing 1.5 g. of potassium carbonate and a small amount of mercury. (Potassium carbonate to repress acidity, mercury to remove excess iodine.) 8.5 g. of silver nitrate (50 mmoles) was added slowly, while the flask was cooled in an ice-bath. The mixture was refluxed for 2 hr., and the crude nitrate was distilled into a flask containing 1.5 g. of potassium carbonate and a droplet of mercury. A small amount of calcium sulfate was added to remove cloudiness (presumably water). A further 7.5 g. (44 mmoles) of silver nitrate was added and the mixture again refluxed for 2 hr. The product was distilled into a cooled tube equipped with a drying tube. The yield was 2.41 g., 83% of theory. (The drying precautions were not observed with the first preparation, samples from which were used for elemental analysis and one mass spectrometric analysis.)

Physical properties: n^{25}_{D} 1.3807, b.p. 87.8–88.0° (cor.).

Anal.[7] Calcd. for $C_2D_5O_3N$ (98% enrichment level): C, 25.06; H + D, 10.25; N, 14.61. Found: C, 24.56; H + D, 9.68; N, 14.18.

Mass Spectrometric Analysis.[8]—Direct analysis of the mass spectrum showed that the sample contained approximately 90% completely deuterated material, 3% with one hydrogen atom per molecule, and a maximum of 5 mole per cent. water. A subsequent analysis of the pyrolysis products indicated a maximum water content of 4 mole per cent. and a minimum enrichment level of 98%.

An unusual, though not unique, feature of the mass spectrum is that the highest mass peak observed contains one hydrogen (or deuterium) atom less than the parent molecule.

Infrared Analysis.[9]—Infrared spectra were obtained for both liquid and vapor and showed the expected shift of the C–H stretching bands. This shift uncovered a previously unnoticed band at 2920 cm.$^{-1}$, which appears to be a combination band of the 1640 and 1280 cm.$^{-1}$ nitrate frequencies.[10]

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(1) A facility owned by the U. S. Government and operated for the U. S. Navy, Bureau of Ordnance, by Hercules Powder Company under Contract NOrd 10431.

(2) R. Steinberger and K. E. Carder, *J. Phys. Chem.*, **59**, 255 (1955).

(3) D. L. Hildenbrand, A. G. Whittaker and C. B. Euston, *ibid.*, **58**, 1130 (1954).

(4) (a) S. F. Boys and J. Corner, *Proc. Roy. Soc.* (*London*), **A197**, 90 (1949); (b) O. K. Rice and R. Ginell, *J. Phys. Colloid Chem.*, **54**, 885 (1950); (c) R. G. Parr and B. L. Crawford, Jr., *ibid.*, **54**, 929 (1950); (d) W. P. Reid, *ibid.*, **57**, 242 (1953).

(5) M. W. Evans, *Chem. Revs.*, **51**, 363 (1952).

(6) Tracerlab, Inc., Boston, Mass.

(7) Micro-Tech Laboratories, Skokie, Ill. Values of %H as received were recalculated on the basis of a 98% enrichment level.

(8) Mass spectrometric analyses were performed by Dr. C. A. Genge, Hercules Experiment Station, Wilmington, Del.

(9) Infrared spectra were measured by R. W. Phillips, this Laboratory.

(10) We are indebted to Dr. Bryce L. Crawford, Jr., University of Minnesota, for this suggestion.