TABLE II

TRANSFER FUNCTIONS OF *n*-AMYL MERCAPTAN IN THE EMULSION COPOLYMERIZATION OF STYRENE AND METHYLMETHACRYLATE

Mole % styrene	0	23.6	48	63	84	100
Transfer Function	0.72	4.9	7.8	9.5	14.3	21.4
			7.0			20.6[a]

[a] Obtained from the data given in Part I[3].

Summary

The rate of reaction of a regulator during the copolymerization of two monomers is discussed theoretically. An experimental investigation of the rate of reaction of *n*-amyl mercaptan in the emulsion copolymerization of styrene and methylmethacrylate gives satisfactory agreement with the theory.

PASSAIC, NEW JERSEY RECEIVED MAY 7, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

The Acid Catalyzed Decomposition of Diazoacetic Ester in Some Aprotic Solvents at 25°

BY ROBERT J. HARTMAN,[1] CLARENCE J. HOCHANADEL[2,3] AND EDWARD G. BOBALEK[1]

It has been suggested by Hantzsch[4] that the comparison of the reaction rates of acid catalyzed decomposition reactions of diazoacetic ester can provide a measure of the protophilic character of different acids. Although the validity of this interpretation has been questioned in some instances,[5,6] the general usefulness of this comparison of relative acid-strengths has been supported by rather convincing arguments.[7]

From the viewpoint of providing a criterion for measuring acidity, the interpretation of some of the earlier data[4,6,8,9,10] was obscured by the complexity of the acid–base systems that were involved as the primary catalytic components. Such complexity is unavoidable when the acid occurs in the presence of a basic solvent or other added protophilic substances.[11,12,13,14] The greatest simplicity can be anticipated for the reaction systems wherein the solvent medium has a minimum tendency to influence the acid–base equilibria of the reactive components, for example, in hydrocarbon solvents.[6,7,8] In these types of systems the acid-catalysis effect should be influenced primarily by the acid–base equilibria involving only the acid catalyst and the diazoacetic ester, and it can be expected that the reaction rates should provide a less-complicated index of relative acidities for the members of a series of similar acid types. However, in view of the fact that hydrogen-bonding or similar types of association effects can occur even in aprotic solvents,[15] it seemed more probable that the effective catalytic properties of any particular acid would vary considerably in different solvents of the simple aprotic class. In fact, it has been demonstrated by Weissberger and Högen[8] that significant differences in reaction rates occurred even in solvents as simple as toluene and hexane. Consequently, it seemed to be a question of some interest to determine the influence of the anticipated solvent effects when this particular reaction-rates method is used to compare relative strengths of acids and bases, and to establish whether this procedure for measuring relative acidity provides results that are consistent with those deduced by other criteria.

Experimental

Reagents.—The diazoacetic ester was prepared according to the method of Fraenkel,[16] which involved the reaction of a pure grade of glycine ethyl ester (Eastman Kodak Company) and C. P. sodium nitrite in aqueous solution, followed by an ether extraction of the diazo reaction product. After the ether extract had been dried for several days with anhydrous calcium chloride, the greater part of the ether was separated by evaporation *in vacuo* at low temperatures, and the residue of ester was purified by distillation *in vacuo* from freshly burned lime at temperatures of 50–60°. The ester was stored over barium hydroxide, and vacuum distilled again as it was required for the preparation of solutions in the various solvents. The purity of the ester was checked frequently during the course of the storage period by measuring the nitrogen yield after decomposition with acid and, in every instance, the experimental results for the material used in the experiments corresponded to the stoichiometric values calculated on the assumption that the ester contained less than 1% of nonmeasurable impurities. The purified diazoacetic ester and its solution in the various solvents remained stable for periods of at least several months.

The solvents used were special pure grades (Eastman Kodak Company) of toluene, chlorobenzene, bromobenzene, iodobenzene, nitrobenzene, *o*-nitrotoluene and *m*-nitrotoluene. These solvents were subjected to some addi-

---

[1] Present address: The Arco Company, Cleveland, Ohio.

[2] Present address: Monsanto Chemical Research Laboratories, Oak Ridge, Tennessee.

[3] This paper is constructed from a dissertation presented by Clarence J. Hochanadel to the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[4] Hantzsch, *Z. Elektrochem.*, **24**, 201 (1918); **29**, 221 (1923); **30**, 194 (1926); *Z. physik. Chem.*, **125**, 251 (1927).

[5] Halban, *Z. Elektrochem.*, **29**, 434 (1923).

[6] Brönsted and Bell, THIS JOURNAL, **53**, 2478 (1931).

[7] Weissberger, *ibid.*, **65**, 245 (1943).

[8] Weissberger and Högen, *Z. physik. Chem.*, **A156**, 321 (1931).

[9] Bredig and Ripley, *Ber.*, **40**, 4015 (1907).

[10] Brönsted and Duus, *Z. physik. Chem.*, **117**, 299 (1925).

[11] Brönsted, *Rec. trav. chim.*, **42**, 718 (1923).

[12] Lowry, *Chem. Ind.*, **42**, 43 (1923).

[13] Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

[14] Luder, *Chem. Rev.*, **27**, 547 (1940).

[15] S. J. O'Brien and co-workers, THIS JOURNAL, **61**, 2504 (1939); **62**, 1189, 2065, 3227 (1940); **63**, 2709 (1941).

[16] Fraenkel, *Z. physik. Chem.*, **60**, 202 (1907).

TABLE I

CONSTANTS THAT DEFINE THE INFLUENCE OF THE ACID CATALYSTS ON THE REACTION RATES

Acid	Solvent	Reaction order n	Acid concentration range, molar	$\alpha \times 10^2$	$\beta \times 10^3$	No. of measurements	Error of k_p, av. dev., %
Iodoacetic	Chlorobenzene	1.74	0.17–0.40	0.535	0.54	4	± 3
Bromoacetic	Chlorobenzene	1.84	.16– .99	2.42	2.14	6	± 2
Chloroacetic	Chlorobenzene	1.79	.22– .69	4.49	5.28	5	± 3
Dichloroacetic	Chlorobenzene	1.45	.033–.25	2550	3100	9	± 8
Bromoacetic	Toluene	1.79	.27– .86	1.34	1.86	5	± 2
Chloroacetic	Toluene	1.88	.25– .80	3.58	2.86	5	± 3
Dichloroacetic	Toluene	1.47	.033–.25	2700	2500	8	± 9
Bromoacetic	Bromobenzene	1.86	.33–1.1	2.64	2.49	5	± 2
Chloroacetic	Bromobenzene	1.86	.11–0.70	5.47	4.57	6	± 5
Dichloroacetic	Bromobenzene	1.28	.036– .27	2500	5200	8	±10
Dichloroacetic	Iodobenzene	1.50	.046– .19	3300	3900	3	±10
Dichloroacetic	Nitrobenzene	1.4	.051– .16	1500	6200	5	± 8
Chloroacetic	Nitrobenzene	1.5	.15–1.2	6.6	45	7	± 4
Bromoacetic	Nitrobenzene	1.5	.40–1.3	4.4	23	5	± 4
Chloroacetic	*o*-Nitrotoluene	1.9	.26–0.83	9.0	10	4	±10
Chloroacetic	*m*-Nitrotoluene	1.3	.15– .97	5.0	30	6	± 7

tional purification according to the procedures described by O'Brien and co-workers.[15]

Pure grades (Eastman Kodak Company) of dichloroacetic, monochloroacetic, bromoacetic and iodoacetic acids were subjected to some additional purification. The dichloroacetic acid was fractionated several times in all Pyrex apparatus, and only the fraction having the boiling point range of 193.5–194.0° was retained from the last distillation. The monochloroacetic and bromoacetic acids were vacuum distilled several times in an all Pyrex system. The iodoacetic acid was crystallized repeatedly from a mixed solvent of ligroin and benzene until the final crystallization product was of a clean, white color. The purified acids were stored in a vacuum desiccator that was charged with sulfuric acid.

Apparatus and Procedure.—Reaction rates were determined by measuring the rate of evolution of nitrogen as manifested by the rate of the increase of the pressure in a constant volume and constant temperature system. The apparatus was a modification of the type developed by Brönsted and Duus.[10] Essentially, it consists of a reaction flask connected to a manometer by means of a glass-spring tube. The 250-ml. reaction flask was an adaptation of the design of Norris and Strain.[17] A 90-ml. cylindrical reservoir was sealed to the bulb of the reaction flask through a stopcock (2 mm. bore), and a pressure equalizing tube connected the top of the reservoir to the neck of the flask. The flask and reservoir were closed by mercury-sealed, but non-lubricated, ground-glass caps. A side arm of the reaction flask was connected to the manometer system by means of a spiral, glass-spring tube. This manometer was similar to that described by King,[18] and with the aid of a magnifying lens, the position of the meniscus could be read to a scale division of ±0.1 mm. The reaction flask was immersed in a water-bath that was maintained at 25 ± 0.005°, and agitated mechanically at the rate of 200 strokes per minute through an amplitude of 2 cm.

The volume of the apparatus was measured by the usual procedure of noting the pressure change when a known volume of gas at constant temperature was expanded into the previously evacuated system. The average of several determinations was 257.0 ± 0.5 ml.

The procedure of measurement of the reaction rates was the following: twenty-five ml. each of the acid and ester solutions in a given solvent were transferred, respectively, to the reservoir and reaction flask, and the system was evacuated for five minutes with a Cenco Hyvac pump while being agitated in the constant temperature bath in order to remove dissolved gases from the reagents.[19] Following this preliminary evacuation treatment, the capillary exit tube that connected the pump to the apparatus was sealed, using an oxygen torch. When the removal of dissolved air had been effected satisfactorily, the manometer readings remained constant in the closed system for at least several minutes. When this condition was realized, the agitation was stopped for the period required to open the stopcock and mix the solutions of the ester and the acid. The initial pressure measurement was taken when one-half of the acid solution had passed through the stopcock and subsequent readings of the pressure were made at intervals of 0.5–10 minutes, depending on the rate of increase of the pressure.

Discussion of Results

The data for the various acid catalyzed decomposition reactions of diazoacetic ester in several aprotic solvents are summarized in Table I, which lists the range of molar concentrations (at 25°) of the catalytic acids, and the values on the constants α and β, as defined by the empirical equation

$$k_p = \alpha C_a^2 + \beta C_a \qquad (1)$$

where C_a is the concentration of the catalytic acid and k_p is the velocity constant of the reaction. The constants α and β were evaluated graphically by plotting k_p/C_a *versus* C_a. Table I lists also the number of measurements used to determine the respective linear functions, together with an estimate of the precision of the results, expressed as the average of the percentage deviations of the individual observed values of k_p from the values calculated by the empirical equation. Examples of some data, typical of the kind used in these calculations, are cited in Table II.

In each instance, the concentration ranges studied were limited by the catalytic effect of the acid, which fixed the conditions at which precise rate

---

[17] Norris and Strain, THIS JOURNAL, **57**, 187 (1935).

[18] King, *ibid.*, **49**, 2689 (1927); **50**, 2089 (1928).

[19] During this de-gassing process some solvent was removed, thereby changing slightly the concentration of the reagents. The maximum correction for this solvent loss was determined gravimetrically after collecting the solvent vapors in a trap cooled by a carbon dioxide–acetone mixture. This small correction was applied to the calculation of the concentration of the two solutions.

TABLE II

VELOCITY CONSTANTS FOR THE DICHLOROACETIC ACID CATALYZED DECOMPOSITION OF ETHYL DIAZOACETATE IN TOLUENE[a]

C_{acid}	C_{ester}	k_p
0.253	0.0249	2.13
.189	.0187	1.53
.142	.0114	0.90
.106	.0105	.58
.0794	.00783	.43
.0594	.00586	.28
.0445	.00439	.14
.0333	.00329	.089

[a] Selected from the complete data contained in Thesis (ref. 3).

measurements were possible. The velocity constants k_p were determined graphically by plotting log $(p_f - p_t)$ *versus* the time in minutes, where p_f represents the stoichiometric value of the final pressure, assuming complete reaction, and p_t is the measured pressure in mm. of mercury at some interval of the reaction time. (The calculated values of p_f were checked experimentally in many instances by allowing time for the reaction to go to completion. The experimental and theoretical values agreed within the limits ±1%, which defines the magnitude of the experimental error.) Several of the rate constants were calculated by the Guggenheim method,[20] and the results agreed with those determined by the graphical procedure that defines the values which fixed the constants that are reported in Table I. In these series of measurements, the concentration of the reactive ester was adjusted to about one-tenth of the acid concentration. It was anticipated that in the presence of a large excess of the acid-catalyst, the virtual course of the diazo-decomposition reaction could be described by the monomolecular rate law. This expectation was realized approximately in the cases of toluene and the halogenated benzenes. However, with the exception of the dichloroacetic acid catalyzed reactions, the ten-fold excess of acid failed to enforce the monomolecular rate law on the reactions in the nitro-solvents. In these instances, a progressive retardation of the rates was observed in the later stages of the reactions, and the velocity constants, k_p, were approximated graphically by computing the maximum slope of the nearly linear initial portions of the pressure–time curves. Since this procedure of calculation is somewhat arbitrary, the data for the nitro-solvents are not strictly comparable with the more regular results in the other solvents. Consequently, these more doubtful data are included in this discussion with explicit reservations as to their correctness, and for the purpose of providing a somewhat qualitative standard of comparison with the measurements in other solvents.

The theory has been advanced that the catalytic action of the acid involves the transfer of a proton between the acid and the reactant substrate.[4,21,22] In the instance of the diazo-decomposition reactions here described, the acid is involved in the reaction (the first order reaction law is approximated only in the presence of a large excess of acid), and experimental evidence favors the assumption that the reaction mechanism involves the formation of a reactive complex between the acid and the ester, followed by a decomposition of the ester through the reaction of the complex with another acid molecule.[6,7,8] An attempt was made to check agreement of these rate measurements with the theoretical mechanism by computing the order of the reaction. Since the rate of reaction of the acid is directly proportional to the diazo-decomposition, it may be assumed that the apparent order of the reaction (n) with respect to the acid concentration (C_a) can be defined by an equation based on the differential method of van't Hoff,[23] namely

$$n = \mathrm{d}\log k_p/\mathrm{d}\log C_a \qquad (2)$$

Table I lists the values of n that were calculated by determining graphically the slopes of the linear functions that were obtained by plotting log k_p *versus* log C_a. Apparently, these calculations failed to establish an integral order that is dependent on the acid concentration. The values of n seem to be influenced by both the nature of the catalytic acid and of the solvent reaction medium, and in no instances do they exceed the value of 2. The decrease of n with the increase of the dissociation tendency of an acid (as measured by the ionization constant in aqueous solution) has been noted previously by other authors.[24] In explanation of the fractional order, hypotheses can be advanced concerning the influence of the association of the acid upon the tendency for the formation of the reactive complex, and it is conceivable that the reaction can occur at different rates with the available monomeric and dimeric acids. Certainly the stronger acids are less dimerized in aprotic solvents.[25] However, this proposition is difficult to prove on the basis of the kinetic data alone, and the results of this investigation do not provide much cause for extending the speculation concerning the reaction mechanism beyond that already discussed by the authors who are cited. The variations in the values of n indicate that the kinetics cannot be interpreted in terms of a consistent and simple mechanism even in the instance of reactions in these supposedly less complex solvents. Some question may remain as to whether this condition provides a serious hindrance to the use of the kinetic method as a measure of the relative acidities of the catalytic acids. It can be established that the uncertainty regarding the mechanism provides

---

(20) Guggenheim, *Phil. Mag.*, [2] **7**, 538 (1926).

(21) Taylor, *Z. Elektrochem.*, **20**, 201 (1914).

(22) Hall, *Chem. Rev.*, **8**, 191 (1931).

(23) Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Company, Inc., New York, N. Y., 1940, p. 1047.

(24) Bell, Lidwell and Vaughan-Jackson, *J. Chem. Soc.*, 1792 (1936).

(25) Bell and Caldin, *ibid.*, 382 (1938).

no serious limitations for this application. A convenient measure of the acid strength is provided by the constant β which represents the limiting value of the ratio k_p/C_a at infinite dilution. Using this standard of comparison, it is apparent that at least a qualitative consistency is maintained when the acid strengths are ordered from the kinetic data in each solvent. Besides establishing agreement for the ordering of the β values in the various aprotic solvents, it is possible to indicate a proportionality between these results and the relative acidity as measured by the dissociation constants for these same acids in aqueous solutions.

This proportionality can be established by considering the empirical relation

$$pK = pK_0 + A\sqrt{\beta} \tag{3}$$

where pK is the negative logarithm of the dissociation constant of the acid in aqueous solution. The constants A and pK_0, as computed by plotting the values of pK for the halogen acids[26,27] as a function of $\sqrt{\beta}$ are listed in Table III. Within the limitations imposed by the small number of data used to test this equation, no deviations from linearity were observed and, at least for this series of acids, the values of pK_0 and A provide an index of the solvent effect on apparent acid strengths. No attempt is made herein to interpret a theoretical explanation for the empirical relation that defines these constants. A limited theoretical approach to the problem has been suggested by other authors.[28,29] If equation (3) is valid, the constant pK_0 can be interpreted as representing a minimum acid strength (measured by thermodynamic methods in aqueous solutions) required of an acid in order that it be effective in promoting an increased rate of decomposition of the diazo compound in the designated aprotic solvent. However, the experimental data now available are too limited for adequate testing of this conclusion.

TABLE III

CONSTANTS FOR THE LINEAR EQUATIONS THAT RELATE THE NEGATIVE LOGARITHMS OF THE AQUEOUS DISSOCIATION CONSTANTS (pK) OF SOME HALOGEN SUBSTITUTED ACETIC ACIDS TO THE CATALYTIC CONSTANTS (β) IN APROTIC SOLVENTS

Solvent →	Chlorobenzene	Toluene	Bromobenzene	Nitrobenzene
pK_0	3.01	2.93	2.93	3.05
A	0.963	1.00	0.720	0.739

In general, it seems that these kinetic methods provide a measure of the acidity of the catalytic acids that is consistent with that deduced by the classical techniques. Moreover, at least for the aprotic solvents, this procedure provides a sensitive measure of the influence of the solvent on the reaction rates. Should it be assumed that the effect of the solvent in accelerating the reaction is related to its basic properties, then it is interesting to note that this reaction rate method provides an ordering of the relative basic strengths of these aprotic solvents that is reasonably consistent with similar comparisons that were deduced by considering the correlation of solubility and infrared absorption measurements on solutions of the halogen acids in these same solvents.[15] That is to say, the greater the basic character of the solvent, the more pronounced is its influence in promoting an increased reaction rate, and the reaction rates method tends to group solvents according to their basicity in a manner that is at least qualitatively in agreement with the interpretations of these other authors.

Summary

Velocity constants were determined for the reaction of diazoacetic ester with dichloroacetic, monochloroacetic, bromoacetic and iodoacetic acids in several aprotic solvents. The kinetic data are interpreted so as to provide a comparison of the relative acid strengths of some of these reactive acids in chlorobenzene, bromobenzene, iodobenzene, nitrobenzene, toluene, *o*-nitrotoluene and *m*-nitrotoluene.

CLEVELAND, OHIO RECEIVED MAY 13, 1946

---

(26) MacInnes, "Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, p. 391.

(27) Richter, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1939, p. 311.

(28) Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924).

(29) Bell, *Proc. Roy. Soc.* (London), **A154**, 414 (1936).