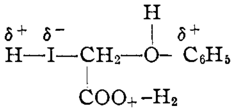

$$\overset{\delta^+}{\mathrm{H}}-\overset{\delta^-}{\mathrm{I}}-\underset{\mathrm{COO_{+}-H_2}}{\underset{|}{\mathrm{CH_2}}}-\overset{\mathrm{H}}{\overset{|}{\mathrm{O}}}-\overset{\delta^+}{\mathrm{C_6H_5}}$$

However, such a doubly charged ion would be certain to have some bulky hydriodic acid molecules or iodide ions closely associated with it near the centers of positive charge. This effect could easily provide some steric hindrance to the proper approach of the entering hydriodic acid or iodide ion and result in high $\Delta H^{\ddagger}$ values. Halogen substitution in the ring, specially if in the *o*-position, should be able to help stabilize the proton on the ethereal oxygen by weak hydrogen bonding and lower $\Delta H^{\ddagger}$ somewhat; fluorine should be better than chlorine in this respect and the data agree. In the same way the loss in entropy in going into the transition state for *o*-fluorine should be greater than for *o*-chlorine because of the greater rigidity imparted to the transition state. For halogen in the *p*-position, the partial hydrogen bonding effect would be absent and only the electrical effects would operate.

TABLE III

HYDROLYSIS RATE CONSTANT FACTORS

Substituted phenoxyacetic acid	k^a 115°, 10^6 sec.$^{-1}$	k^b 100°, 10^6 sec.$^{-1}$	Ea, kcal.	log pZ, 100°	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u., 100°	$\Delta F^{\ddagger}$, kcal.
None	10.85^c	2.23	30.4	12.12	29.6	− 5.5	31.7
2-F	9.14	2.23	27.1	10.20	26.3	−14.3	31.6
4-F	10.87	2.36	29.3	11.53	28.6	− 8.2	31.7
2,4-diF	10.14	2.42	27.5	10.48	26.7	−13.0	31.6
2-Cl	8.90	2.01	28.5	11.02	27.8	−10.6	31.7
4-Cl	7.61	1.74	28.3	10.82	27.6	−11.5	31.9
2,4-diCl	6.68^d	1.61^e	27.3	10.19	26.6	−14.3	31.9

^{a} Average deviations ≈ 0.6. ^{b} Average deviations ≈ 0.08. ^{c} Average of 10.82 and 10.89. ^{d} Average of 7.63 and 5.72. ^{e} Average of 1.32 and 1.90.

A Hammett plot of the data *vs.* σ-values gives a scatter of points. However, as discussed by Jaffé,[6] the slope of the line from a 4-halophenoxyacetic acid to phenoxyacetic acid should be the same as that from a 2,4-dihalophenoxyacetic acid to a 2-halophenoxyacetic acid. For F, at 115° the values are 0.013 and 0.74; at 100°, 0.40 and 0.58. For Cl, at 115°, the values are −0.68 and −0.55; at 100°, −0.48 and −0.43. Except for the case of F at 115°, the agreement is fair.

Although the data do not fit a Hammett plot, a plot of $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$ gives a straight line. A least squares fit gave a slope of 125° and an intercept of 32 kcal. If the slope is taken as the "isokinetic temperature"[7] at which the Hammett relationship fails, the temperatures selected for the study of the reaction were not the best possible choice. However, it is of interest that the linear relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ holds for the *o*-substituted acids as well as for the non-*o*-substituted materials.

This work was supported by a contract with the U. S. Army Chemical Corps., Fort Detrick, Frederick, Md.

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[6] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[7] J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

LOS ANGELES 7, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

The Hydrazinolysis of Methyl Acetate

BY ROBERT N. WASHBURNE, JOHN G. MILLER AND ALLAN R. DAY

RECEIVED JUNE 2, 1958

The reaction of methyl acetate and hydrazine in benzene solution in the presence of methanol has been studied. The reaction was first order in both hydrazine and ester when the molar ratio of ester to hydrazine was 1:2, but became first order in ester and second order in hydrazine at ratios of 1:1 and 2:1.

In previous work the catalytic effects of hydroxylated solvents on the rates of hydrazinolysis of ethyl acetate were determined.[1] The energies and entropies of activation for these reactions were calculated also. In that work the ratio of ester to hydrazine was 1 mole to 2 moles in every case and the reactions followed second-order kinetics, being first order with respect to each of the reactants. In the present study of the hydrazinolysis of methyl acetate, it was decided to follow the reactions dilatometrically. As long as the ratio of ester to hydrazine was maintained at $1M:2M$, the reactions were second-order. When the ratio was changed to $2M:1M$, the reaction order changed and the dilatometric method became inapplicable. As a result, a chemical titration method was utilized. In this way it was found that the reactions became third order when the ratio of ester to amine was $1M:1M$ and $2M:1M$. In these cases the reactions were first order with respect to the ester and second order with respect to the hydrazine.

Solvents of the type *n*-hexane and cyclohexane would have been desirable for these reactions because of the non-solvating nature of these solvents. The insolubility of hydrazine in these solvents rendered them useless, however, and benzene was finally chosen as solvent. Even with benzene it was found that a minimum of 5 M methanol was necessary to achieve homogeneity. While this imposed certain limits on the system, it had certain advantages also. For example, it made it possible to observe the effect of methanol on the reaction rates. The use of methanol rather than some other alcohol avoided any complication of the reaction kinetics which might otherwise have occurred as the result of ester interchange. Molar ratios, ester to hydrazine, of 1:2, 1:1 and 2:1 were used and the methanol concentration was varied from 5 M to 19.1–21.4 M (pure methanol).

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[1] R. A. Ferren, J. G. Miller and A. R. Day, THIS JOURNAL, **79**, 70 (1957).

Experimental

It had been planned originally to follow the reactions dilatometrically. Because of the change in order from second to third order, it became necessary to use a chemical method for much of the work. During the course of the present work it was possible to compare the physical and chemical methods for following the reaction.

Apparatus.—The dilatometers were constructed entirely of Pyrex glass. The volume of the reaction chambers was approximately 90 ml. and the attached measuring tubes in which the volume changes were observed were of 2 mm. precision-bore capillary tubing about one meter in length. These tubes were jacketed to permit thermostating and the constancy of the bore was checked cathetometrically using a length of mercury. A two-way stopcock led into the reaction chamber through a mercury-seal-off bulb, permitting entrance of the reaction mixture and subsequent sealing with mercury. The thermostat surrounding the reaction chamber was held at 30 ± 0.01°

The burets, pipets, volumetric flasks and thermometers were carefully calibrated.

Reagents.—Benzene, analytical grade, was distilled over sodium, b.p. 80°, $n^{25}D$ 1.4985. Methanol, absolute analytical grade, was treated with a small amount of sodium and distilled, b.p. 64.8°, $n^{25}D$ 1.3270. Methyl acetate, analytical grade, was dried over magnesium sulfate and distilled, b.p. 56.6°, $n^{25}D$ 1.3538. Anhydrous hydrazine was obtained from 95% hydrazine by distilling several times from excess barium oxide, b.p. 113–113.5°.

Procedure.—Owing to the polar nature of hydrazine, stock solutions of this reagent had to be prepared in methanol rather than in benzene. Two stock solutions were used. In one a 10-ml. aliquot contained 0.1 mole of hydrazine and 0.166 mole of methanol and in the other a 10-ml. aliquot contained 0.2 mole of hydrazine and 0.087 mole of methanol. Benzene was used as the solvent for methyl acetate. In this case 10 ml. contained 0.10 mole of methyl acetate.

The same method was used for preparing the reaction mixtures for both the dilatometric and titration methods. A suitable aliquot of the hydrazine stock solution was measured into a volumetric flask. The proper amount of methanol was added from a buret, and then benzene to an approximate volume of 80 ml. An aliquot of the methyl acetate stock solution now was added and the flask filled to the mark with benzene. In those cases where no benzene was used, the methyl acetate was weighed into the volumetric flask. Methanol then was added to an approximate volume of 80 ml., an aliquot of the hydrazine stock solution was added and the flask filled to the mark with methanol.

(a) **Dilatometric Method.**—The reaction mixture was fed into the dilatometer by force of gravity until the reaction chamber was filled up to the bottom of the capillary measuring tube. Mercury next was allowed to flow into the seal-off bulb, forcing the reaction solution into the measuring tube and sealing the system when the cock was closed. It was found convenient to place a thread of mercury on top of column of liquid in the measuring tube to prevent evaporation and to aid in reading the height of the column. The solutions contracted in volume due to reaction and the height of the column diminished. The constancy of the final reading was checked over a 6-hour period.

(b) **Chemical (Titration) Method.**—The procedure was essentially the same as the method which was reported earlier.[1]

Calculations and Results

The well-known method of Guggenheim[2] for determination of the velocity constants of first-order reactions may be extended to second-order reactions. For the dilatometric measurements reported here, let $h_1, \ldots h_i, \ldots h_n$ be a series of cathetometer readings taken at times $t_1, \ldots t_i, \ldots t_n$, and $h_1', \ldots h_i', \ldots h_n'$ be taken at times $t_1 + \tau, \ldots t_i + \tau, \ldots t_n + \tau$, each a constant time τ after one of the previous set. It may be shown[3] that a plot of the common logarithm of the quantity $(h_i - h_i')/[(h_i - h_\infty)(h_i' - h_\infty)]$ against time should be a straight line for a second-order reaction and its slope multiplied by $2.303/[a(1 - c)]$ should equal k_2, the rate constant. Here, a is the initial concentration of the reactant in excess and c is the ratio of the concentration of the other reactant to a. Good straight lines were obtained by this procedure for all the second-order rates reported in Table I.

TABLE I

VELOCITY CONSTANTS FOR THE REACTION BETWEEN HYDRAZINE AND METHYL ACETATE IN BENZENE–METHANOL AND METHANOL SOLUTIONS AT 30°

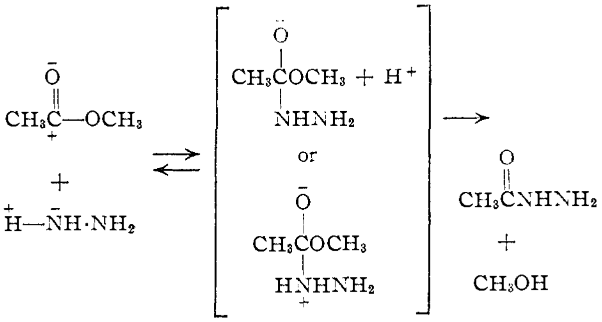
Ester, moles/l.	Hydrazine, moles/l.	Ester/hydrazine	Methanol, moles/l.	Average velocity constant $k \times 10^5$	Order of reaction
1.00	1.990	0.503	5.0	2.53[a]	2[b]
0.99	1.948	.511	5.0	3.25[a]	2[c]
1.00	1.990	.503	7.0	3.36[a]	2[b]
0.99	1.990	.500	10.0	4.69[a]	2[b]
1.00	1.973	.507	10.0	4.42[a]	2[c]
1.00	1.990	.503	12.0	5.31[a]	2[b]
0.99	1.980	.500	21.4(pure)	25.70[a]	2[b]
1.00	1.990	.503	21.4(pure)	25.60[a]	2[b]
1.99	1.841	1.084	5	1.97[d]	3[c]
1.99	1.846	1.081	10	2.33[b]	3[c]
1.80	1.691	1.064	18.8(pure)	12.50[d]	3[c]
1.98	0.950	2.084	5	1.22[d]	3[c]
2.00	0.990	2.020	5	1.05[d]	3[c]
1.99	0.956	2.087	10	1.53[d]	3[c]
1.95	0.887	2.198	19.1(pure)	8.17[d]	3[c]

[a] In units of moles/liter-second. [b] Dilatometric method. [c] Titration method. [d] In units of moles²/liter²-second.

For the rates determined chemically, the second-order constants, k_2, were calculated in the usual way from the relationship $dx/dt = k_2(a - x)(b - x)$ and the third-order constants, k_3, from the relationship $dx/dt = k_3(a - x)^2(b - x)$, where a was the initial concentration of hydrazine and b that of the ester. The expression $dx/dt = k_3(a - x)(b - x)^2$ was not obeyed in any case.

Discussion

The mechanism for the second-order hydrazinolysis of ethyl acetate was discussed in a previous paper.[1] Ignoring solvent effects the mechanism for the hydrazinolysis of methyl acetate may be written as



In the earlier work the hydrazine was in excess and the reactions followed second-order kinetics. This has been confirmed in the present study. However a change to third-order kinetics takes place

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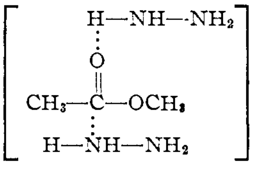
(2) E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

(3) Unpublished work, W. S. Wartel, K. A. Simon and J. G. Miller, "A Tau-Period Method of Determining Second-Order Reaction Rates," delivered at the meeting of the American Chemical Society, Atlantic City, September, 1952.

when the ratio of ester to hydrazine is 1:1 or 2:1. The fact that the reaction is second order with respect to the hydrazine when the ester is in excess is interesting. Whether this change from second order to third order is dependent only on the change in concentrations of the ester and hydrazine cannot be answered at present. There is some possibility that the methanol may play a role in the change in order. Unfortunately this could not be determined in the present work since it was not possible to study the various ratios of ester to hydrazine in benzene solution in the absence of methanol. The latter was necessary to maintain homogeneity.[4]

The simplest conceivable transition state for the third-order reaction would be



$$\left[\begin{array}{c} H{-}NH{-}NH_2\\ \vdots\\ O\\ \|\\ CH_3{-}C{-}OCH_3\\ \vdots\\ H{-}NH{-}NH_2 \end{array}\right]$$

This picture disregards the fact that the ester is in excess. It should be more applicable in those systems where the hydrazine is in excess. In the latter cases, the reactions had second-order kinetics. In some way then it would appear that the methanol is partly responsible for the change in kinetic order. No amount of methanol, however, will cause the change to third-order kinetics when the ratio of ester to hydrazine is 1:2. The ratio of reactants is the most important single factor, although the methanol plays an important part at that point where the hydrazine is no longer in excess.

As the ester becomes equivalent to the hydrazine and finally is present in excess, it becomes apparent that some equilibrium, governing the availability of hydrazine or ester, is disturbed. This could account for the diminished reaction rate as the reaction becomes third order. This disturbance is not observed when the hydrazine is in excess. On the basis of the present data, it is reasonable to suppose that hydrogen bonding of one of the reactants with methanol is responsible for the disturbance. In view of the fact that it has not been possible to study the reaction in the absence of methanol it has been decided to postpone discussion of proposed mechanisms for the effects observed. Such discussion will be included in the next paper in the series. At that time data will be available from a study of aminolysis reactions also.

PHILADELPHIA, PENNA.

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[4] Recent work in our laboratory on the aminolysis of methyl acetate gives a similar change in order from second to third. In this case methanol plays a definite role in the change.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND THE RADIOCARBON LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Allylic Rearrangements. XLIII. Some Studies of the Thermal Decomposition of Allyl Chlorosulfinate-1-C^{14}[1]

BY S. H. SHARMAN,[2a] F. F. CASERIO,[2b] R. F. NYSTROM, JOHN C. LEAK AND W. G. YOUNG

RECEIVED MAY 24, 1958

Allyl chlorosulfinate-1-C^{14} has been decomposed thermally to allyl chloride and sulfur dioxide in a variety of solvents. Through the use of special experimental techniques, the chlorosulfinate ester has been decomposed with quantitative allylic rearrangement in the solvent *n*-decane and with varying degrees of preservation of structure in other solvents. Qualitative rate data for the reaction in several solvents also are presented. A mechanism involving a rate-determining alkyl–oxygen ionization is discussed.

Introduction

The reaction of thionyl chloride with various substituted allyl alcohols has been examined under a variety of conditions in these laboratories,[3] and the resulting data have indicated that the decomposition of the intermediate chlorosulfinate ester is extremely complex in nature. In order to study more thoroughly the reactions of this intermediate, attention recently has been focused upon the allyl system itself ($CH_2{=}CHCH_2{-}$). Aside from the reduction of the allylic system to its simplest form, the present investigation offers the added advantage, peculiar in the allylic field to this system, that the chlorosulfinate ester of allyl alcohol is a stable, isolable compound. The decomposition reaction may thus be examined directly without interference from the by-product of the reaction of thionyl chloride with alcohol, namely, hydrogen chloride. Due to the symmetry properties involved, radiocarbon labeling of the chlorosulfinate was required.

A preliminary experiment, reported in 1953,[4] suggested that allyl chlorosulfinate-1-C^{14} ($CH_2{=}CHC^{14}H_2OSOCl$) decomposes without added solvent at approximately 90° to give allyl chloride containing 51% 1-C^{14}. As a consequence of several subsequent experiments, summarized in Table I, it became evident that, in the absence of tertiary amine bases or their hydrochlorides, the results of such decomposition reactions could not be duplicated under the usual operating conditions. It also became clear that the addition of even trace

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[1] This work was supported in part by a grant to W. G. Young from the National Science Foundation.

[2] (a) Standard Oil Co. of California Research Fellow, 1956–1957; (b) Standard Oil Co. of California Research Fellow, 1952–1953.

[3] (a) R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 813 (1956); (b) W. G. Young, F. F. Caserio and D. Brandon, *Science*, **117**, 473 (1953); (c) W. G. Young, F. F. Caserio, R. H. DeWolfe and G. Dennis, THIS JOURNAL, **77**, 4182 (1955); (d) W. G. Young and F. F. Caserio, unpublished work.

[4] R. F. Nystrom and J. C. Leak, THIS JOURNAL, **75**, 3039 (1953).