TABLE I

EVOLUTION OF CARBON DIOXIDE FROM DEHYDROASCORBIC ACID AND ASCORBIC ACID–FORMALDEHYDE SOLUTIONS

Molar acetate buffer, *p*H 5.4, was used; ascorbic acid 9.65×10^{-2} *M* in buffer; cupric acetate (oxidant) 0.193 *M* in buffer; formaldehyde 10% in buffer; temperature 40°

Minutes	Dehydroascorbic[a] acid		Formaldehyde[b] ascorbic acid	
	Microliters of carbon dioxide			
30	90	95	34	34
60	138	144	121	116
90	219	225	222	222
120	282	290	298	296
270	543	547	593	586
450	752	759	798	795
720	964	973	940	937

[a] 1.0 ml. of buffer plus 0.5 ml. of cupric acetate in body of Warburg flask; 0.5 ml. of ascorbic acid in sidearm. [b] 0.5 ml. of buffer plus 1.0 ml. of formaldehyde in body; 0.5 ml. of ascorbic acid in sidearm.

bon dioxide evolution is similar in both systems. As shown previously[2] ascorbic acid and formaldehyde react to yield carbon dioxide at 32 and 40°, evolution beginning at zero time. However, at 25° there is a two hour delay in the evolution of carbon dioxide. The same phenomenon has been noted with solutions of dehydroascorbic acid prepared in the same way and at the same concentrations as described above.

These experiments strongly suggest that formaldehyde is reduced by ascorbic acid and that the resultant dehydroascorbic acid slowly forms carbon dioxide as one of its decomposition products.

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Solvolytic Reactivities of Some Secondary Alkyl Chlorides

BY JOHN D. ROBERTS[1]

Despite numerous comparisons of the reactivities of saturated organic halides toward nucleophilic reagents[2] relatively few investigations have been made of solvolytic reactivities of saturated halides under comparable conditions except for the series: methyl, ethyl, isopropyl, and *t*-butyl.[2] Dostrovsky and Hughes[3] have measured the solvolytic reaction rates of several alkyl bromides in aqueous alcohol and formic acid while Bartlett and Swain[4] and Brown and Johanneson[5] have reported relative reactivities for tertiary chlorides.

In the present investigation the solvolytic reaction rates of four saturated secondary alkyl chlorides were measured in 50% water–50% alcohol by volume at 90–100° and are summarized in Table I.

TABLE I

SOLVOLYTIC REACTION RATE CONSTANTS OF SATURATED ALKYL CHLORIDES

Chloride	$k_1^{90°}$, hr.$^{-1}$	$k_1^{95°}$, hr.$^{-1}$	$k_1^{100°}$, hr.$^{-1}$	$\Delta H^{\ddagger}$, kcal.[a]	(95°) % olefin
Isopropyl	0.0582	0.0934	0.135	22.8	..
s-Butyl	.0539	.0891	.139	25.6	..
Diethylcarbinyl[b]	.0539	.0825	.122	22.1	15
Methylisopropyl carbinyl[c]	.159	.253	.386	24.3	24

[a] Average over 90–100°, obtained graphically. [b] Prepared by the method of Hass and Weber, *Ind. Eng. Chem., Anal. Ed.*, **7**, 231 (1935). [c] Prepared by the method of Whitmore and Johnston, Ref. 6.

The reactivities of the first three compounds given in Table I are very similar as might be expected from their structures. The somewhat greater reactivity of methylisopropylcarbinyl chloride may be related to the rearrangement which probably takes place in the hydrolysis of this substance.[6] The difference in reactivity is hardly due to bimolecular elimination (E2) involving solvent molecules since no significant difference in the extent of olefin formation is noted between diethylcarbinyl and methylisopropylcarbinyl chlorides. No noticeable trend in the values of $\Delta H^{\ddagger}$ is apparent for this series of chlorides. It is probable that further elucidation of the relative reactivities of secondary halides will depend on whether or not quantitative determination of the relative fractions of ionization (S_N1) or direct (S_N2) mechanisms involved in solvolysis reactions can be made by methods such as proposed by Grunwald and Winstein.[7]

Experimental

The rate determinations were carried out in 50% water–50% alcohol (by volume) as previously described[8] using an oil-thermostat with a mercury–toluene regulator. Temperatures were accurate to ±0.1°. The extent of olefin formation was measured by quantitative hydrogenation of larger scale runs than were used in the rate experiments. In each case the reactions were carried to a calculated 95% or more of complete solvolysis before determination of olefin. The procedure was as follows. A solution of the alkyl halide in 100 ml. of 50% alcohol was placed in a 250-ml. distilling flask along with a thin-walled bulb containing a weighed quantity of platinum oxide and a number of 3–4 mm. glass beads. The contents of the flask were degassed and the flask sealed *in vacuo*. After the solvolytic reaction was complete, the tip of the seal-off of the flask was scratched and inserted in a short plastic tube leading to a hydrogen buret. The line was evacuated and the tip broken by carefully flexing the plastic tube. Hydrogen was admitted from the buret, the catalyst bulb broken by vigorous shaking, and the reduction

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[2] For many references see Evans, "The Reactions of Organic Halides in Solution," The Manchester University Press, Manchester, 1946, and Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940.

[3] Dostrovsky and Hughes, *J. Chem. Soc.*, 164 (1946).

[4] Bartlett and M. Swain, unpublished work, presented by P. D. Bartlett at the Organic Symposium, Boston, 1947.

[5] H. C. Brown and Johanneson, paper presented at the Atlantic City meeting of the American Chemical Society, April, 1946.

[6] Whitmore and Johnston, THIS JOURNAL, **55**, 5020 (1933).

[7] Grunwald and Winstein, *ibid.*, **70**, 846 (1948).

[8] Roberts, Urbanek and Armstrong, paper submitted for publication in THIS JOURNAL.

carried until no further hydrogen was absorbed. The hydrogen uptake was corrected for catalyst absorption.

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Some Keto-Enol Equilibria in the Gas Phase

BY ROBERT SCHRECK[1]

Conant and Thompson[2] have measured the positions of the keto-enol equilibria for several 1,3-dicarbonyl compounds in the gas phase. In the work reported below, similar data have been obtained for the two further tautomeric systems: ethyl cyclopentanone-2-carboxylate and ethyl cyclohexanone-2-carboxylate. For purposes of comparison, ethyl acetoacetate has also been reexamined in the gas phase, and all three of the esters named have been studied in the liquid state.

Procedures

The samples of the esters were equilibrated in the vapor phase in the way that was developed by Conant and Thompson.[2] The only significant departures from the original procedure were, in fact, (1) that the condensate from the slow low-pressure distillation was collected in a tube cooled with liquid nitrogen (−196°), rather in one cooled with solid carbon dioxide (−80°); and (2) that the contents of the distilling flask were kept thoroughly mixed by stirring with a glass-enclosed nail, which was magnetically rotated at 300 r. p. m., rather than by shaking. That equilibrium was indeed attained was shown, as in the work of Conant and Thompson, by the fact that successive fractions of the distillate showed essentially identical properties.

The "low-enol" ethyl acetoacetate that had been equilibrated in the liquid state was analyzed by the familiar indirect bromine titration of K. H. Meyer, with the use of diisobutylene for the removal of the excess bromine. The "high-enol" ethyl acetoacetate that had been equilibrated in the gas phase was analyzed by comparing its measured refractive index $n^{20}\text{D}$ with a curve drawn to represent Beyaert's empirically determined relation between refractive index and composition.[3] The two cyclic esters, equilibrated both in the liquid state and in the gas phase, were analyzed by Meyer's direct bromine titration.

Results

The results of the measurements described above are collected in the accompanying table. It will be noted that small, but significant, discrepancies exist between the values found in this investigation and those reported in the earlier literature. These discrepancies presumably indicate the order of magnitudes of the unavoidable uncertainties that must be expected in such work. It will also be noted that the abnormally high enol content of ethyl cyclohexanone-2-carboxylate in the liquid state is retained, and in fact increased in the gas phase.

TABLE I

KETO-ENOL EQUILIBRIA IN THREE β-KETOESTERS

			% enol at 25°[b]			
Ester	State	No. of runs[a]	Range	Average value	Standard dev.	Lit.
Ethyl	Liquid	3	7.38– 7.41	7.39	0.01	7.4[c,d]
acetoacetate	Gas	9	46.6 –51.6	49.3	1.6	45.3–46.9[e]
Ethyl cyclopentanone-	Liquid	3	4.55– 4.65	4.60	0.04	4.45[c,f]
2-carboxylate	Gas	7	26.7 –28.3	27.5	0.5	....
Ethyl cyclohexanone-	Liquid	4	72.9 –74.5	73.7	0.6	76.0[c,f]
2-carboxylate	Gas	7	89.9 –91.7	90.6	0.6	....

[a] A number of runs which were made while the procedures were being perfected are omitted from this table. [b] In the measurements reported in this paper, the equilibria with the liquid esters were attained at room temperature, which was considered to be sufficiently close to 25°; the equilibria with the gaseous esters were attained by keeping the distilling flask in an oil thermostat held at 25 ± 0.2°. [c] At 20°. [d] K. H. Meyer, *Ber.*, **45**, 2843 (1912). [e] J. B. Conant and A. F. Thompson, Jr., THIS JOURNAL, **54**, 4039 (1932). [f] W. Dieckmann, *Ber.*, **55**, 2470 (1922).

Materials

Ethyl acetoacetate (Carbide and Carbon Chemicals Corporation, technical grade) was washed with distilled water, dried over an excess of anhydrous copper sulfate, dried further over Drierite, and then distilled at 12–15 mm. pressure. The observed refractive index, $n^{20}\text{D}$ 1.4191, agreed with Beyaert's value[3] for the equilibrium ester (7.4% enol).

Ethyl cyclopentanone-2-carboxylate and ethyl cyclohexanone-2-carboxylate were prepared by the procedures described in "Organic Syntheses."[4] At equilibrium, the refractive index $n^{20}\text{D}$ of the liquid cyclopentanone derivative, 1.4519, was in complete agreement with the value reported by Van Rysselberghe.[5] On the other hand, that of the cyclohexanone derivative, 1.4779, was in poor agreement with value of 1.4750 for $n^{17.5}\text{D}$, reported by Feofilaktov[6]; for this reason, special pains were taken to ensure that the compound was pure and that equilibrium had actually been reached. The freshly distilled ("high-enol") material with $n^{20}\text{D}$ equal to 1.4819 was allowed to

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[1] This paper was written on the basis of the laboratory notebooks and incompleted Master's thesis which were left by Robert Schreck at his untimely death.—G. W. WHELAND.

[2] J. B. Conant and A. F. Thompson, Jr., THIS JOURNAL, **54**, 4039 (1932).

[3] M. Beyaert, *Natuurw. Tijdschr.*, **18**, 209 (1936).

[4] "Organic Syntheses," Coll. Volume 2, A. H. Blatt, editor, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 116ff and 531ff, respectively.

[5] M. van Rysselberghe, *Bull. sci. acad. roy. Belg.*, [5] **11**, 171 (1926).

[6] V. V. Feofilaktov, *Bull. acad. sci. U. R. S. S. Classe sci. chim.* 521 (1941); *C. A.*, **37**, 2347 (1943).