[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF EMORY UNIVERSITY]

Rate of Oxime Formation of Some Aryl Alkyl Ketones[1]

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The reaction of carbonyl compounds with semicarbazide, hydroxylamine and phenylhydrazine has been extensively investigated.[2] All of these investigations had one thing in common—the reactions were all run reversibly in a buffered aqueous-organic medium.

We wish to report the results of rate studies run irreversibly in an essentially anhydrous medium. We have studied the rate of oxime formation of seven phenyl alkyl ketones and seven *p*-xylyl alkyl ketones, at three temperatures in a medium consisting of 2 *M* pyridine, 0.5 *M* pyridine hydrochloride in methanol.

Materials.—The methanol was J. T. Baker C. P. special used without further purification. The *p*-xylyl alkyl ketones were prepared and purified as previously described.[3] The phenyl propyl and higher phenyl alkyl ketones were synthesized by a standard procedure.[4] The other reactants and solvents were purchased from the Paragon Division of the Matheson Company. The pyridine hydrochloride was prepared by treating an ether solution of pyridine with dry hydrogen chloride gas, filtering, washing repeatedly with dry ether and storing in a vacuum desiccator.

Procedure.—The method of measurement was essentially that of Ölander[5] involving the determination of the unreacted hydroxylamine by means of an excess of iodine and back titration with sodium thiosulfate. Carbon tetrachloride was used as an indicator. Standard solutions corresponding to every 10% stage of the reaction from 0 to 100% were prepared and the empirical iodine titer established. In actual practice a standard curve was constructed, plotting ml. of thiosulfate against moles of hydroxylamine present. This curve was used to determine the extent of the reaction. The normalities of the iodine and thiosulfate solutions were checked frequently and new standard curves constructed when changes in normality were observed. Duplicate samples were determined in each case and the value of k determined on each duplicate by the method of least squares. The values recorded for k are the average values for the duplicates. The duplicate values checked for each other within 10% in all cases and within 5% in a large majority of the cases. The phenyl ketones were run using 0.05 *M* solutions of ketone and 0.05 *M* solutions of hydroxylamine hydrochloride. In the case of the *p*-xylyl ketones the concentrations were 0.2 *M* ketone and 0.1 *M* hydroxylamine hydrochloride. It has been pointed out that changes in concentration do not change the value of k.[2c] The pH of each of the four solutions corresponding to 0 and 100% reaction for each series of ketones was measured in a Beckmann meter, using a glass electrode.[6] The observed value was 4.1 ± 0.1 (av. of 10 readings on each solution). The values of k obtained are recorded in Table I.

TABLE I

RATES OF REACTION OF KETONES WITH HYDROXYLAMINE HYDROCHLORIDE AT THREE TEMPERATURES

	Rate constants in liters/mole/sec. × 10^3					
	Phenyl[a]			*p*-Xylyl[b]		
Alkyl	$k_{30°}$	$k_{35°}$	$k_{40°}$	$k_{30°}$	$k_{35°}$	$k_{40°}$
Methyl	24.6	26.9	48.8	1.84	3.10	4.03
Ethyl	14.5	18.4	30.3	0.863	1.10	1.62
Propyl	10.6	14.7	21.5	.579	0.792	1.20
Butyl	11.7	16.7	21.5	.523	.878	1.19
Amyl	10.7	16.7	21.5	.566	.847	1.15
Hexyl	12.2	18.2	23.9	.558 .542[c]	.846	1.17
Heptyl	11.5	17.8	22.2	.552	.850	1.05

[a] 0.05 *M* ketone, 0.05 *M* hydroxylamine hydrochloride.
[b] 0.20 *M* ketone, 0.10 *M* hydroxylamine hydrochloride.
[c] 0.10 *M* ketone, 0.10 *M* hydroxylamine hydrochloride.

The irreversible nature of the reaction has been confirmed. If the data from the reactions are treated in the usual graphical manner, plotting time against $x/a(a - x)$ for the phenyl series and time against log $(a - x)/(b - x)$ for the *p*-xylyl series, straight lines are obtained. A sample of acetophenone oxime was allowed to stay in a medium corresponding to 100% reaction for a total of sixteen hours. Aliquots failed to show any hydroxylamine present at any time during this period. If any of the ketones was allowed to react for as long as sixteen hours, values corresponding to 95 to 98% reaction were always obtained. The rate values obtained by this method follow the usual pattern for an homologous series in each of the two groups of ketones. The difference in rate observed between the two series is also consistent with the general behaviour of ortho-substituted aromatic aldehydes, ketones and acid derivatives. Further work along this line is being pursued.

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Summary

1. The rate of oxime formation of fourteen aryl alkyl ketones has been determined.

2. The rate constants obtained at 30, 35 and 40° are given.

3. The medium for determining the rates by an irreversible reaction is described.

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(2) An excellent summary of previous work is given by Conant and Bartlett, THIS JOURNAL, **54**, 2881 (1932). Other pertinent articles include: (a) Westheimer, *ibid.*, **56**, 1962 (1934); (b) Anziani, *Bull. soc. chim.*, **6**, 949 (1939); (c) Stempel and Schaffel, THIS JOURNAL, **66**, 1158 (1944); Kadesch, *ibid.*, **66**, 1207 (1944).

(3) Lester and Suratt, *ibid.*, **71**, 2262 (1949).

(4) Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 3.

(5) Ölander, *Z. physik. Chem.*, **129**, 1 (1927).

(6) The medium employed in these measurements is a modification of one used for the quantitative determination of aldehydes and ketones *cf.* Bryant and Smith, THIS JOURNAL, **57**, 57 (1935).