Experimental Results and Discussion

As seen from Fig. 1, fatty acids are adsorbed on Raney cobalt in a manner somewhat similar to that found for nickel, although a higher concentration is necessary to form a monolayer. The number of moles of behenic (C_{22}) acid adsorbed per unit weight of nickel is the same within experimental error as that for palmitic acid (C_{16}). Experiments with fatty acids of shorter chain length were even more subject to errors due to formation of soluble cobalt soaps than were those with palmitic acid. The surface area of the cobalt catalyst calculated by assuming a cross section of 20.5 Å.[2] for the adsorbed acid is 15.6 square meters per gram, which is a little less than the value usually obtained for Raney nickel.

The total aluminum content of the cobalt catalyst was found to vary between 3.3 and 2.7% depending on whether a single batch of alkali was employed or whether the aluminum was removed from the alloy by treatment with several fresh batches of alkali at 10-minute intervals. Raney nickel prepared under similar conditions analyzed around 11% total aluminum.

Hydrogen content studies with Raney cobalt indicated that hydrogen was present in the freshly prepared catalyst, but not to the extent found in Raney nickel. Values obtained on several samples ranged from 40 to 70 standard milliliters of hydrogen per gram of cobalt. The hydrogen is held rather tightly by the cobalt. Pumping at room temperature for 0.5 hour removed only about 6% of the total hydrogen. Upon flaming the decomposition bulb with a Bunsen flame, the remaining hydrogen was given off. A rapid explosion was not obtained as in the case with Raney nickel. Residual hydrogen determinations showed that 99% of the total hydrogen was removed in this manner.

The hydrogenation of benzene over freshly prepared Raney cobalt was found to proceed slowly at 120° with the rate becoming fairly rapid at 150° or above. The rate was found to be first order in hydrogen pressure and independent of the quantity of benzene placed in the bomb. Plots of the logarithm of hydrogen pressure against time gave good straight lines with the exception of slight curvature during the first minute or two of the reaction when freshly prepared catalyst was employed. As the catalyst aged, the kinetic behavior deviated from strictly first-order behavior. The activation energy was found to be approximately 23 kcal. per mole in the range 155–180°. At 160°, $k_{1.0} = 4.65 \times 10^{-5}$ sec.$^{-1}$ for 1 l. hydrogen volume and 1 g. of catalyst.

A Comparison of Raney Nickel and Raney Cobalt Catalysts.—Raney cobalt is somewhat easier to prepare than Raney nickel in that the removal of alkali by washing can be accomplished rather quickly with the cobalt while a lengthy washing procedure is required for nickel. The aluminum content is some 10–12% for nickel but only around 3% for cobalt. The surface area as measured by fatty acid adsorption is somewhat smaller than for nickel; the acid is more strongly held in the nickel, while benzene-soluble compounds are formed with the cobalt. This difficulty can be fairly well overcome by the use of very long chain acids. The hydrogen content of the cobalt is less than for nickel, but the hydrogen appears to be more strongly bound. The hydrogenation activity of the cobalt catalyst as measured by its ability to effect the addition of hydrogen to benzene is less than that of nickel. However, the activation energy is greater for the cobalt so that the differences in activity become less as the temperature increases. The lower activity of the cobalt may well be caused by the firmer bonding of hydrogen to the cobalt. As the temperature is raised, the hydrogen becomes more readily available, and hence the activity is increased.

THE KINETICS OF THE DECOMPOSITION OF MALONIC ACID IN AROMATIC AMINES

By Louis Watts Clark

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Kinetic studies have been reported on the decarboxylation of malonic acid in aqueous solution,[1] as well as in several non-aqueous solvents including glycerol,[2] dimethyl sulfoxide,[2] triethyl phosphate,[3] quinoline[4] and aniline.[5] Apparently, no kinetic study of the decomposition of malonic acid in pyridine has been reported. Preliminary experiments in this Laboratory having revealed that malonic acid is smoothly decarboxylated in pyridine solution at temperatures near 100°, the kinetics of the reaction were carefully investigated for the sake of comparison with other aromatic amines.

Since the decomposition of malonic acid in aniline proceeds quite slowly at 80 and 100° (the temperatures at which the experiments reported[5] were performed), further studies were made at higher temperatures. Results of these investigations are reported herein.

Experimental

Reagents.—The reagents used were (1) reagent grade malonic acid; (2) reagent grade aniline, boiling range 183–186°; (3) reagent grade pyridine, boiling range 114–116°.

Apparatus and Technique.—The apparatus and technique in this study were the same as those used in studying the decomposition of malonic acid in triethyl phosphate.[3]

The Decomposition of Malonic Acid in Pyridine and Aniline.—At the beginning of each experiment 100 ml. of the amine (saturated with dry CO_2 gas) was placed in the reaction flask in the thermostat oil-bath. A sample of malonic acid weighing either 0.1764 g. in the case of pyridine or 0.1810 g. in the case of aniline (the amount required to produce 38.0 and 39.0 ml. of CO_2, respectively, on complete reaction) was placed in a thin glass capsule and introduced at the proper moment into the solvent in the usual manner. The rapidly rotating mercury sealed stirrer immediately crushed the capsule, the contents dissolved and mixed in the solvent, and reaction began. The course of the reaction was followed in the usual manner.

(1) G. A. Hall, Jr., *J. Am. Chem. Soc.*, **71**, 2691 (1949).

(2) L. W. Clark, This Journal, **60**, 825 (1956).

(3) L. W. Clark, *ibid.*, **60**, 1150 (1956).

(4) P. E. Yankwich and R. L. Belford, *J. Am. Chem. Soc.*, **75**, 4178 (1953).

(5) Y. Ogata and R. Oda, *Bull. Inst. Phys. Chem. Res. (Tokyo)*, *Chem. Ed.*, **23**, 217 (1944); *C. A.*, **43**, 7904 (1949).

<div align="center">TABLE I</div>

<div align="center">DECOMPOSITION OF MALONIC ACID IN AROMATIC AMINES, KINETIC DATA</div>

System	E^* (cal.)	A (sec.$^{-1}$)	Temp. coeff.	$\Delta H\ddagger$ (cal.)	$\Delta S\ddagger$ (e.u.)	$\Delta F\ddagger_{140}°$ (cal.)	$k_{(140°)}$ (sec.$^{-1}$)
1. Malonic acid	34,500	1.8×10^{14}	2.72	33,000	$+ 4.5$	31,100	0.00024
2. Malonic acid plus quinoline	18,500	2.57×10^{7}	1.78	17,800	-27.0	24,300	.00364
3. Malonic acid plus aniline	22,850	6.32×10^{9}	2.01	22,800	-14.3	28,700	.0050
4. Malonic acid plus pyridine	26,600	1.59×10^{12}	2.75	26,000	$+ 7.2$	23,000	.0126

The above procedure was repeated at five different temperatures between 98–114° in the case of pyridine, and at six different temperatures between 126–144° in the case of aniline. The total volume of carbon dioxide obtained in each experiment was 100% of the theoretical yield within the limits of error of the experiment. Duplicate and triplicate runs at each temperature gave reproducible results.

Results and Discussion

A plot of log $(a - x)$ vs. t in the case of each amine at each temperature studied gave excellent straight lines, indicating that the decomposition of malonic acid in pyridine and in aniline is a first-order reaction. From the slopes of the lines thus obtained the specific reaction velocity constants for the reaction in the two solvents at the various temperatures studied were calculated. For the case of the decomposition of malonic acid in pyridine the temperatures studied and the corresponding specific reaction velocity constants obtained in sec.$^{-1}$ were as follows: 98.2°, 0.000335; 102.3°, 0.000496; 107.0°, 0.000764; 110.9°, 0.00111; 113.5°, 0.00141. Results for the case of the decomposition of malonic acid in aniline were as follows: 126.6°, 0.00184; 131.8°, 0.002735; 135.7°, 0.00358; 138.6°, 0.00437; 141.8°, 0.00550; 144.1°, 0.00640.

A straight line was obtained in each case when log k was plotted against $1/T$ according to the Arrhenius equation. From the slopes of the lines thus obtained the activation energy and the frequency factor for the reaction in each solvent were calculated. On the basis of the Eyring equation the enthalpy of activation, entropy of activation and free energy of activation at 140° for the reaction in each solvent were calculated. The kinetic data for the reactions studied are summarized in Table I which includes also for comparison data for molten malonic acid[6] and for malonic acid in quinoline.[4]

Some insight into the role of the solvent may be gained by considering the data in Table I. A comparison of the data in lines 1 and 2 shows that quinoline effects a very large lowering of the enthalpy of activation as well as a large decrease in the entropy of activation of the reaction with respect to molten malonic acid. This results in a lowering of the free energy of activation, so that, at this temperature (140°), malonic acid decomposes 15 times as fast in quinoline as it does alone. A comparison of lines 1 and 3 reveals that aniline lowers the enthalpy of activation by a large amount and also lowers the entropy of activation considerably, resulting in a small decrease in the free energy of activation at 140° with respect to molten malonic acid. Malonic acid decomposes 21 times as fast in aniline at

(6) C. N. Hinshelwood, J. Chem. Soc., 117, 156 (1920).

140° as it does alone. A comparison of lines 1 and 4 reveals that pyridine lowers the enthalpy of activation less than does aniline and *increases* the entropy of activation, so that the probability of the formation of the activated state of malonic acid is greater in pyridine than in the molten state. The free energy of activation is lower in pyridine than in any other solvent shown. At 140° malonic acid decomposes 52 times as fast in pyridine as in the molten state.

This order of increasing efficacy of the amines follows the order of increasing basicity as well as the order of decreasing molecular complexity of the solvent.

Studies on the decarboxylation of acetonedicarboxylic acid in aniline[7] have been explained on the basis of the formation of an intermediate unstable compound between reactant and solvent molecules. The decomposition of malonic acid in non-aqueous solvents has been explained on the basis of decarboxylation of the undissociated form of the acid.[5] Results reported herein strongly suggest the possibility that intermediate compound formation may be involved in the case of the decomposition of malonic acid in aromatic amines. The active methylene hydrogen atoms could attach to the unshared electrons on nitrogen. The greater the availability of the electrons the greater would be the probability of the formation of the activated state, other factors being equal. The electron structure of the molecule being thus distorted decarboxylation could occur at either carboxyl group. Results obtained in non-nitrogenous, non-aqueous, basic type solvents[2,3] are in harmony with this view.

Further work on this problem is contemplated.

(7) E. O. Wiig, THIS JOURNAL, 32, 961 (1928).

THE PROTONATION OF N-METHYLACETAMIDE

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Mizushima, *et al.*,[1] have reported that N-methylacetamide (I) in aqueous hydrochloric acid has an absorption peak at 2695 Å., which is not present in the absence of acid. This new absorption was attributed to the formation of the ion II, since

(1) S. Mizushima, T. Simanouti, S. Nakagura, K. Kuratani, M. Tsuboi, H. Baba and O. Fujioka, J. Am. Chem. Soc., 72, 3490 (1950); S. Mizushima, Adv. Prot. Chem., 9, 299 (1954); S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954, p. 118.