position reported does not coincide with that of a definite molecular complex. According to Fig. 4 benzene forms a complex containing one mole of benzene per mole of aluminum bromide which has a decomposition pressure of approximately 2.0 cm. at 15°. The system is homogeneous for molar ratios of $C_6H_6/AlBr_3$ of approximately 5.0 and above. For molar ratios less than 5.0 the complex precipitates at 15°. Ulich[10] has reported molecular weight values for aluminum bromide in benzene ranging from 511 to 463 in the molal concentration range of from 0.3 to 0.040. In contrast to these values, this Laboratory, using the freezing point method, has obtained reproducible values of 534.0 for concentrations as low as 0.0820 molal. This determination is extremely sensitive to traces of moisture, which fact may well account for the results of Ulich. These results would indicate, therefore, that the complex $Al_2Br_6 \cdot 2C_6H_6$ does not dissociate appreciably in this concentration range.

**Acknowledgment.**—The author wishes to express his indebtedness to Mr. Harry E. Crawford for valuable assistance rendered in connection with some of these experiments.

## V. Summary

1. Addition compounds of methyl or ethyl bromide with aluminum bromide are not indicated from vapor pressure–composition diagrams. In benzene a complex is formed having a composition corresponding to 1 mole of $C_6H_6$ per $AlBr_3$.

2. Aluminum bromide is monomeric in ethyl bromide and dimeric in benzene indicating that the addition compound is $Al_2Br_6 \cdot 2C_6H_6$.

3. Electrolysis of alkyl halide solutions of aluminum bromide indicates that this salt behaves as a normal 1–3 electrolyte in these solutions.

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(10) Ulich, *Z. physik. Chem.*, Bodenstein Festband, 323 (1931).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

# Polarographic Acetamide–Formaldehyde and Benzamide–Formaldehyde Kinetic Studies

BY GEORGE A. CROWE, JR.,[1] AND CECIL C. LYNCH

In previous papers[2,3] we showed polarographically that the reaction between urea and formaldehyde to form monomethylolurea was reversible, and studied the effects of change in temperature and *p*H on the reaction. A study of the initial reaction kinetics of formaldehyde with amides having only one amino group (to form methylolamides) seemed desirable. Acetamide and benzamide were selected as typical amides.

The kinetic studies described here indicate that in the initial reaction of formaldehyde with acetamide or benzamide, the equilibrium constant and the energy of activation are about the same as for urea–formaldehyde.[3] The first part of the reaction is second order. The reaction rates at high *p*H values of formaldehyde with acetamide and with urea are about the same, but the reaction of formaldehyde with benzamide is several times as rapid, due to the activating influence of the phenyl group and consequent increase in rate of anion formation of the amide.

## Experimental

The apparatus, general technique and most of the chemicals were as described previously.[2,3] The acetamide was Baker and Adamson, Reagent, m. p. 81°. The benzamide was Eastman Kodak Co., white label, m. p. 130°. The supporting electrolytes consisted of 0.05 *N* lithium hydroxide (*p*H 12.7), 0.1 *M* sodium carbonate (*p*H 11.2) and 0.1 *M* sodium bicarbonate (*p*H 8.6). The supporting electrolyte solutions were made up to twice the concentrations given above. For the test solutions, 3 ml. of the supporting electrolyte was diluted with 1 (or 2) ml. of the amide solution and 2 (or 1) ml. of the formaldehyde solution. The rate constants and equilibrium constants were determined by following the concentration of unreacted formaldehyde with time, using the polarograph.

Reaction rates and equilibrium constants for the reversible amide-formaldehyde reactions are given in Tables I and II. The reactions were found to be second order.

**Effect of Temperature Change.**—The energy of activation for the acetamide–formaldehyde reaction was found to be 13,850 cal. per mole at *p*H 12.7. For the benzamide–formaldehyde reaction the activation energy was 14,950 cal. per mole at *p*H 11.2. It is felt that the energies of activation are accurate to ±1 kcal. per mole. These values are in the same range as the energy of activation for the urea–formaldehyde (to monomethylolurea) reaction, for which Crowe and Lynch[3] obtained 15,900 cal. per mole at *p*H 12.7, and Smythe[4] found 14,700 cal. per mole in neutral solution. Thus it appears, as postulated earlier,[3] that the increase in reaction rate with increase in temperature is not dependent on the kind of amide to any appreciable extent, but instead upon the increased rate of dehydration of methylene glycol (hydrated formaldehyde) with increasing temperature.

**Effect of *p*H Change.**—In the *p*H range between 8.6 and 12.7, the reaction rate increases with hydroxyl ion concentration, although the equilibrium constant remains at about the same

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(1) Hercules Powder Company, Hercules Experiment Station, Wilmington, Delaware.

(2) Crowe and Lynch, THIS JOURNAL, **70**, 3795 (1948).

(3) Crowe and Lynch, *ibid.*, **71**, 3731 (1949).

(4) Smythe, *J. Phys. Colloid Chem.*, **51**, 369 (1947).

TABLE I

RATES FOR THE REACTION OF ACETAMIDE WITH FORMALDEHYDE TO FORM METHYLOLACETAMIDE

| Temp., °C. | *p*H | Acetamide, *M* | Formaldehyde, *M* | *k*, l. mole$^{-1}$ sec.$^{-1}$ | Equil. const., *K* |
|---|---|---|---|---|---|
| 25.0 | 12.7 | 0.0355 | 0.00355 | 0.0286 | 24.8 |
| 25.0 | 12.7 | .0178 | .00355 | .0282 | 23.4 |
| 25.0 | 12.7 | .00710 | .00355 | .0274 | 21.8 |
| 25.0 | 12.7 | .00355 | .00355 | .0277 | 24.0 |
| 25.0 | 11.2 | .0889 | .00889 | .00252 | 31.7 |
| 25.0 | 8.6 | .0889 | .0889 | $8.5 \times 10^{-6}$ | 21.4 |
| 15.0 | 12.7 | .0355 | .00355 | 0.0134 | .. |
| 20.0 | 12.7 | .0355 | .00355 | .0244 | 25.9 |
| 30.0 | 12.7 | .0355 | .00355 | .0444 | 18.0 |

TABLE II

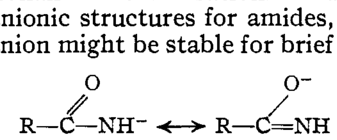
RATES FOR THE REACTION OF BENZAMIDE WITH FORMALDEHYDE TO FORM METHYLOLBENZAMIDE

| Temp., °C. | *p*H | Benzamide, *M* | Formaldehyde, *M* | *k*, l. mole$^{-1}$ sec.$^{-1}$ | Equil. const., *K* |
|---|---|---|---|---|---|
| 25.0 | 12.7 | 0.0142 | 0.00355 | 0.0955 | 22.8 |
| 25.0 | 12.7 | .00710 | .00355 | .0930 | 20.7 |
| 25.0 | 12.7 | .00355 | .00355 | .105 | 23.0 |
| 25.0 | 11.2 | .0355 | .00889 | .0157 | 24.0 |
| 25.0 | 8.6 | .0355 | .0355 | $7.5 \times 10^{-5}$ | 20.2 |
| 15.0 | 11.2 | .0355 | .0355 | 0.00605 | .. |
| 20.0 | 11.2 | .0355 | .0355 | .00712 | .. |
| 30.0 | 11.2 | .0355 | .0355 | .0239 | .. |

value, within experimental error. The increase of reaction rate with increase of *p*H in this region is probably due to two factors: increase in the dehydration rate of methylene glycol, and an increase in the amount of anionic form of the amide, as discussed for the urea–formaldehyde reaction.[3]

It is believed, for several reasons, that the *anion* of the amide is the activated form which reacts with dehydrated formaldehyde: (a) Smythe[4] observed that when 8 *M* solutions of urea and formaldehyde of *p*H 7.0 were mixed, the hydrogen ion concentration increased immediately by several hundred-fold, and an appreciable amount of formaldehyde reacted. As the reaction progressed (to form monomethylolurea), the hydrogen ion concentration slowly diminished.

(b) Resonance considerations indicate two possible anionic structures for amides, suggesting that the anion might be stable for brief periods

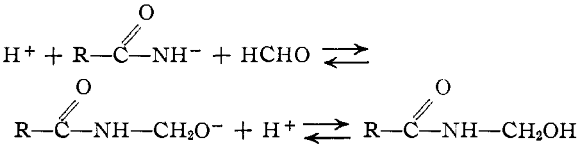


$$\mathrm{R{-}C({=}O){-}NH^-} \longleftrightarrow \mathrm{R{-}C(O^-){=}NH}$$

(c) An electron-attracting group (such as a phenyl group) attached to a carboxylic acid, an amide or a ketone, exerts an inductive effect, and causes increased proton dissociation and anion formation. Resonance in the phenyl group tends to augment the inductive effect. In carboxylic acids, the effect is observed in the ionization constants; for acetic acid the ionization constant is $1.8 \times 10^{-5}$ at 25°, for benzoic acid it is $7.3 \times 10^{-5}$. In amides, the inductive effect can be observed by comparing reaction rates. At 25° and *p*H 12.7, the reaction rate constant of formaldehyde with acetamide is 0.028 sec.$^{-1}$; with benzamide it is 0.096 sec.$^{-1}$. At *p*H 11.2, the benzamide–formaldehyde reaction rate constant was 6.2 times that of the acetamide–formaldehyde reaction; at *p*H 8.6, it was 8.8 times.

(d) Polarographic formaldehyde wave-height measurements compared with urea–formaldehyde reaction rates showed that the reaction rates increased more with increase in hydroxyl ion concentration than with increase in temperature, for a given polarographic formaldehyde wave-height increase. This suggested that for hydroxyl ion increase, there was an increase in the activated form of urea as well as an increase in the dehydration rate of formaldehyde.[3]

As a result of the above considerations, a mechanism of the generalized amide–formaldehyde reaction has been formulated.



$$\mathrm{H^+ + R{-}C({=}O){-}NH^- + HCHO} \rightleftarrows$$
$$\mathrm{R{-}C({=}O){-}NH{-}CH_2O^- + H^+} \rightleftarrows \mathrm{R{-}C({=}O){-}NH{-}CH_2OH}$$

## Summary

In the reversible reactions of acetamide–formaldehyde and benzamide–formaldehyde to form methylolamides, kinetic studies show that the equilibrium constants and energies of activation are about the same as for the urea–formaldehyde reaction to form monomethylolurea. The forward reactions are bimolecular. While the reaction rate of acetamide–formaldehyde reaction is about the same as for urea–formaldehyde reaction at *p*H 12.7 and 25°, the benzamide–formaldehyde reaction is 3.4 times as rapid, due to the inductive effect of the phenyl group. The reaction rate increases as hydroxyl ion concentration increases over the range *p*H 8.6 to 12.7; the equilibrium constant does not vary significantly over this range.

A mechanism for the amide–formaldehyde reaction is proposed, which involves combination of dehydrated formaldehyde with the anion of the amide.

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