then determines a value of f and Equation (B) gives the corresponding value of I_1; together they give a point on the curve for the given value of Θ.

Summary

When the differential equation connecting temperature with time in an exothermic gas reaction is integrated, a sudden temperature rise, corresponding to an explosion, is found to be indicated above a certain sharply defined pressure. From curves of this type, an approximate method for calculating the induction period in thermal explosions has been obtained, and has been applied to the explosions of azomethane and ethyl azide. Rough values of the heats of decomposition of these compounds are thereby obtained. A discussion is given of the rate at which a gas not reacting exothermically comes into thermal equilibrium when admitted to a heated vessel.

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[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Hydrogenation of Carbon Dioxide and a Correction of the Reported Synthesis of Urethans

BY MARK W. FARLOW AND HOMER ADKINS

In an attempt to prepare N-pentamethylene salicylamide through the reaction of methyl salicylate and piperidine at 250° under hydrogen, Wojcik and Adkins[1] obtained a product which they reported as phenyl N-pentamethylene urethan, *i. e.*, $C_6H_5OC(O)NC_5H_{10}$. They suggested that the supposed urethan might be formed through the decarboxylation of salicylic acid followed by the reaction of phenol, carbon dioxide and piperidine. They apparently confirmed this hypothesis by obtaining the same product from phenol, carbon dioxide and piperidine as from methyl salicylate and piperidine. A further study of the postulated reaction has shown that the alleged urethan was a mixture of phenol and formylpiperidine, $C_5H_{10}NC(O)H$. An equimolecular mixture of these two compounds has a constant and narrow boiling range about 10° higher than either component and shows an analysis for nitrogen very nearly the same as for the urethan. Similarly, the products reported as phenyl N-*n*-amyl and *n*-butyl-N-pentamethylene urethans have been found to be mixtures of formyl amines with phenol or butanol-1.

The identification and isolation of formylamines from the reaction products of hydrogen, carbon dioxide, amines and alcohols led to a study of the hydrogenation of carbon dioxide. The significant numerical results are given in the table and may be summarized as follows.

The hydrogenation of carbon dioxide to formic acid in the presence of an amine takes place at 80° or less over Raney nickel.

$$CO_2 + H_2 \longrightarrow HCO_2H$$
$$HCO_2H + RNH_2 \longrightarrow HCO_2NH_3R$$

For example, after one hour at 80° 1-Ph-2-aminopropanol-1 was converted to the formate in a yield of 55% based upon the amine, the carbon dioxide and hydrogen being in excess. The rate and temperature necessary for hydrogenation apparently varies with the structure of the amine as well as with the catalyst. At a sufficiently high temperature (250°) sheet brass, such as has been used in this Laboratory for fabricating liners for steel reaction vessels, is an active catalyst for the hydrogenation. If the hydrogenation is carried out at a temperature much above 100° in the presence of a primary or secondary amine, the formate is dehydrated and the amide (formylamine) is obtained.

$$HCO_2NH_3R \longrightarrow HC(O)NHR + H_2O$$

Since a variety of substances may be present under the conditions used for the hydrogenation, it is not possible to formulate with certainty the course of the reaction. Carbon dioxide might react with a primary or secondary amine with the formation of a carbamate

$$2R_2NH + CO_2 \longrightarrow R_2NC(O)ONH_2R_2$$

or since traces of water are present a carbonate might be formed

$$R_2NH + CO_2 + H_2O \longrightarrow (R_2NH_2)_2O_2CO$$

Dehydration of the carbonate would give the

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[1] Wojcik and Adkins, THIS JOURNAL, **56**, 2461 (1934).

TABLE I

HYDROGENATION OF CARBON DIOXIDE IN PRESENCE OF AMINES[a]

	T, °C.	Time, hours	G. catalyst	Moles	Yield of products
2,2,6,6-Tetra-Me-4-OH piperidine (in EtOH)	100	6	5 Ni(R)	0.10	57% formate of amine
2,2,6,6-Tetra-Me-4-OH piperidine (in EtOH)	100	3	5 Ni(R)	.10	47% formate of amine
Piperidine (in EtOH)	150	9	5 Ni(R)	.25	76% N-formyl-piperidine[b]
n-Amylamine (in EtOH)	150	5	5 Ni(R)	.25	45% N-formyl-*n*-amylamine
1-Ph-2-aminopropanol-1 (in EtOH)	80	1	5 Ni(R)	.04	55% formate of amine
α-Oximinopropiophenone (in EtOH)	80	1	5 Ni(R)	.10	[c]Formate of 1-Ph-2-NH_2-propanol-1
N-*n*-Bu-2-Me-piperidine (in EtOH)	100	6	5 Ni(R)	.10	[c]Formate of amine
Piperidine (in phenol)	250	5	Brass	.50	50% N-formylpiperidine
β-Ph-Et-amine (in phenol)	250	4	Brass	.50	35% N-formyl-β-Ph-Et-amine
n-Amylamine (in phenol)	250	5	Brass	.50	33% N-formyl-*n*-amylamine

[a] Carbon dioxide was admitted to the amine dissolved in EtOH or PhOH until the pressure was constant at about 60 atm. Hydrogen was admitted until the total pressure was 100 to 200 atm. The bomb was then heated to the indicated temperature, the pressure being then 200 to 400 atm. [b] The percentage yield as given is based upon analysis for nitrogen of the product which was made up of the formylpiperidine and phenol. [c] Formic acid was identified but the formate was not isolated in sufficient purity to justify the calculation of a % yield.

TABLE II

PROPERTIES AND ANALYSES OF PRODUCTS

			Analyses, %			
			Carbon		Hydrogen	
Name	B. p. or m. p., °C.	Formula	Calcd.	Found	Calcd.	Found
N-Formyl-*n*-amylamine	124–125 (10 mm.)	$C_6H_{13}NO$	62.6	62.4	11.39	11.31
N-Formyl-β-phenylethylamine	180–181 (14 mm.)	$C_9H_{11}NO$	72.4	72.4	7.45	7.54
N-N′-Di-*n*-amyl urea	88 (m. p.)	$C_{11}H_{24}N_2O$			N, 14.00	14.01
β-Phenylethylamine formate	128–129 (m. p.) (dec.)	$C_9H_{13}NO_2$	64.7	64.65	7.84	7.89
2,2,6,6-Tetramethyl-4-hydroxypiperidine formate	207 (m. p.) (dec.)	$C_{10}H_{23}NO_2$	59.1	59.2	10.43	10.35
1-Phenyl-2-aminopropanol-1 formate	160 (m. p.) (dec.)	$C_{10}H_{15}NO_3$	60.9	60.8	7.69	7.67

carbamate and further dehydration a disubstituted urea. The latter type of product was actually isolated in two instances. The action of hydrogen upon these various types of compounds might well result in the formation of a formyl amine. However, since formates were obtained even with primary amines and since a tertiary amine was as effective as primary and secondary amines in facilitating the hydrogenation of carbon dioxide there seems no reason to assume that the amine plays any other role than to neutralize the formic acid produced by direct hydrogenation.

The formyl derivatives reported in Table I were isolated by fractionation of the reaction mixture through a Widmer column. These various formyl derivatives showed the physical properties and analyses given in Table II. Formylpiperidine[2] was also identified through the preparation of a double salt with mercuric chloride, m. p. 147–148°. The derivative was prepared by heating 5 g. of mercuric chloride and 1 ml. of formylpiperidine in 100 ml. of water until solution was complete. The derivative crystallized out upon cooling the solution and was recrystallized from a mixture of ethyl acetate and petroleum ether. Since formylpiperidine and phenol cannot be separated by fractional distillation the mixture was dissolved in alkali and the amide extracted with ether. The mercuric chloride derivative was then prepared from the material extracted by ether.

The formates were isolated by crystallization from mixtures of alcohol and ether or alcohol and ethyl acetate. Because of the solubility of these salts the yields reported in Table I are in all cases considerably less than the amount of amine formate produced. This is especially true of the formate of 1-Ph-2-amino-propanol-1. The formates were identified by analysis and by comparison with authentic specimens prepared from equimolecular quantities of amine and formic acid in ether.

Diamyl urea $(C_5H_{11}NH)_2CO$ (4.5 g.) and *sym*-diphenylethyl urea[3] $(C_6H_5CH_2CH_2NH)_2CO$ (5.0 g.) were isolated from the reaction products of the last two experiments recorded in Table I.

Summary

Carbon dioxide may be hydrogenated to formic acid in the presence of a variety of amines. If the hydrogenation is carried out at a temperature much above 100°, the formate of the amine may be dehydrated to the substituted formamide.

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(2) Bischler and Napieralski, *Ber.*, **26**, 1908 (1893).

(3) Thiele and Pickard, *Ann.*, **309**, 200 (1899).