

total pressure of O<sub>2</sub> above the reaction was just the total pressure minus 50 Torr. The stirring speeds were adjusted to avoid making the rates diffusion controlled. In rates higher than about 150 M min<sup>-1</sup> diffusion rates of oxygen begin to compete as rate-limiting steps. All kinetic studies were done below this limiting rate.

**Products.**—Reaction solutions were quenched by pouring into cold 1 M HCl. The mixture was extracted with two portions of benzene and the benzene extracts were washed several times with water. The benzene solutions were dried and analyzed by gas chromatography. Fluorene, fluorenone, and fluorenol were determined on an XE-60 column at 230° using chloronaphthalene as an internal standard. No fluorenol was found in any reactions.

9,9'-Bifluorenyl was analyzed on an XE-60 column (seasoned overnight at 275°) at 245°.

**Spectra.**—Visible spectra were done using a Cary 14 spectrophotometer. A Varian Aerograph instrument was used for esr spectra except for liquid helium temperatures, where a super heterodyne spectrometer operating near 9200 MHz was used.

**Registry No.**—Fluorene, 86-73-7; CuOBz, 14604-51-4; Cu(Cl)(OCH<sub>3</sub>), 2850-63-7; Cu(OBz)(OCH<sub>3</sub>), 34825-83-7; (trien)Cu(OBz)(OCH<sub>3</sub>), 34825-62-2; Cu(OCH<sub>3</sub>)<sub>2</sub>, 1184-54-9; (CH<sub>3</sub>CHOCH<sub>2</sub>NH<sub>2</sub>)Cu(OBz), 34825-84-8.

## The Chemistry of Blocked Isocyanates. II. Kinetics and Mechanism of the Reaction of Dibutylamine with Phenyl and 2-Methylphenyl Oxime Carbamates<sup>1</sup>

AARON W. LEVINE\* AND JOHN FECH, JR.

RCA Corporation, David Sarnoff Research Center, Princeton, New Jersey 08540

Received January 24, 1972

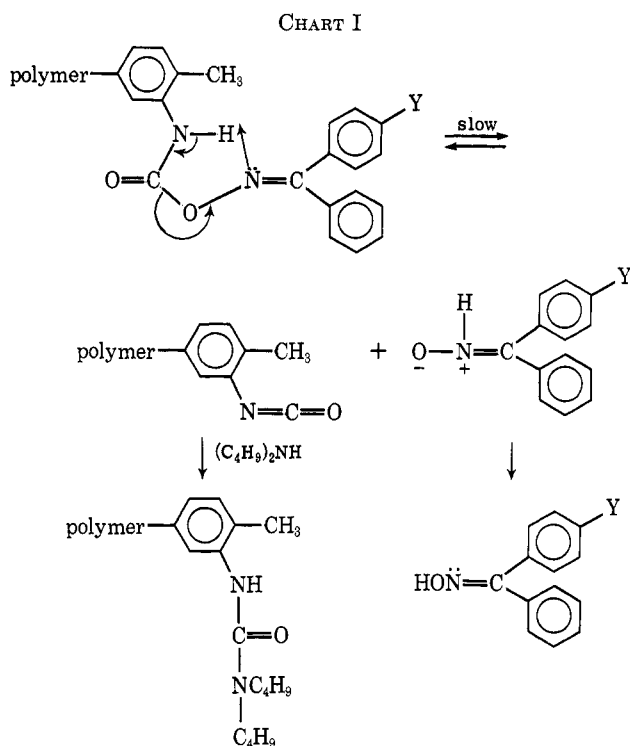
Dibutylamine reacts with carbamates derived from substituted benzophenone oximes and phenyl isocyanates. The reactions follow first-order kinetics and the products are the corresponding substituted phenyldibutylureas and the oximes. The rate constants for reaction of para-substituted phenyl carbamates are insensitive to added excess amine. Activation parameters for the unsubstituted compound are  $\Delta H^\ddagger = 25.7 \pm 0.3$  kcal mol<sup>-1</sup> and  $\Delta S^\ddagger = -0.24 \pm 0.39$  eu. The reaction is facilitated by electron-withdrawing isocyanate substituents ( $\rho = +0.296 \pm 0.012$ ,  $r = 0.995$ , correlation with  $\sigma$ ) and by electron-donating oxime substituents ( $\rho^+ = -0.401 \pm 0.011$ ,  $r = 0.997$ , correlation with  $\sigma^+$ ). The rate constants for carbamates derived from 2-methylphenyl isocyanate and substituted benzophenone oximes also increase with increased electron-donating ability of the substituents ( $\rho = -0.512 \pm 0.034$ ,  $r = 0.979$ , correlation with  $\sigma$ ). The difference in mode of the substituent effect is interpreted as indicating the intervention, in the former case, of a zwitterionic intermediate in the otherwise concerted carbamate dissociation.

In a previous communication,<sup>1</sup> we reported on the unblocking of benzophenone oxime-blocked polyurethanes using dibutylamine as coreactant. It was found that the reaction followed first-order kinetics and was not subject to base catalysis. Unlike the similar reaction of phenol-blocked polyurethanes<sup>2,3</sup> whose rates are favored by electron-withdrawing substituents on the blocking group, the reaction studied was found to be accelerated by electron-donating oxime substituents. On the basis of this evidence and the near-zero entropy of activation for this reaction, we postulated a five-center cyclic, intramolecular transition state for the decomposition as shown in Chart I.

In order to investigate further the postulated mechanism, we undertook to study oxime unblocking of model compounds. Two series of compounds, based on phenyl and 2-methylphenyl isocyanate (Charts II and III) were synthesized. Rate constants were determined for reaction of these compounds with dibutylamine in toluene solution. This paper discusses the results of these experiments and their bearing on the intramolecular transition state.

### Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared (ir) spectra were taken in KBr using a Perkin-Elmer Model 457 instrument. Nuclear Magnetic



Resonance (nmr) spectra were recorded on a Joelco Minimar at ambient temperature in perdeuterioacetone solution. Tetramethylsilane (also deuterated solvents from Stohler Isotope Chemicals) was used as internal standard. Microanalyses were by Micro-Analysis, Inc., Wilmington, Del.

Benzophenone, substituted ketones, hydroxylamine hydrochloride, phenyl isocyanate, and 2-methylphenyl isocyanate were used as received from Eastman Organic Chemicals. Pyridine and dibutylamine were distilled from KOH. All inorganic

(1) Part I: A. W. Levine and J. Fech, Jr., *J. Org. Chem.*, **37**, 1500 (1972). The present paper was presented in part at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 9-14, Abstract ORGN-160.

(2) S. Peterson, *Justus Liebigs Ann. Chem.*, **562**, 205 (1949).

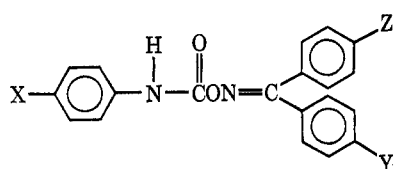
(3) G. R. Griffin and L. J. Willwerth, *Ind. Eng. Chem., Prod. Res. Develop.*, **1**, 265 (1962).

TABLE I  
 SYNTHESIS OF BENZOPHENONE OXIMES

Para substituent	Yield, %	Recrystn solvent	Mp, °C			Estimated syn/anti <sup>a</sup> (by nmr)
			Found <sup>a,b</sup>		Lit. (ref) <sup>c</sup>	
H	95	Methanol	143.5–144.5		144	
NO <sub>2</sub>	51	Aqueous	115–116	syn	115	40/60
		ethanol	136–143	anti	158	
Cl	36	Ethanol	94	syn	95	5/95
			156–159	anti	155–156	
CH <sub>3</sub>	85	Aqueous	118–120	syn	115–116	15/85
		methanol	138–145	anti	153–154	
OCH <sub>3</sub>	79	Methanol	116–120	syn	115–116	50/50
			137–142	anti	137–138	
(CH <sub>3</sub> ) <sub>2</sub> N	87	Methanol	156–159	syn	163	
				anti	176 (6)	40/60
4,4-Bis(CH <sub>3</sub> ) <sub>2</sub> N	74	Benzene	216–219		216–217 (4)	

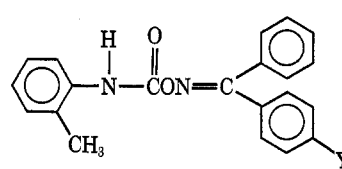
<sup>a</sup> Syn and anti with respect to the substituted aromatic ring. <sup>b</sup> Two distinct melting ranges were frequently observed. <sup>c</sup> Unreferenced values taken from Beilstein.

CHART II



Compd	Substituents		
	X	Y	Z
1	H	H	H
2	NO <sub>2</sub>	H	H
3	Cl	H	H
4	OCH <sub>3</sub>	H	H
5	H	NO <sub>2</sub>	H
6	H	Cl	H
7	H	CH <sub>3</sub>	H
8	H	OCH <sub>3</sub>	H
9	H	N(CH <sub>3</sub> ) <sub>2</sub>	H
10	H	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>
11	NO <sub>2</sub>	OCH <sub>3</sub>	H

CHART III



Compd	Substituent
12	H
13	NO <sub>2</sub>
14	Cl
15	CH <sub>3</sub>
16	OCH <sub>3</sub>
17	N(CH <sub>3</sub> ) <sub>2</sub>

TABLE II

SYNTHESIS OF BENZOPHENONE OXIME PHENYL CARBAMATES<sup>a</sup>

Compd	Mp, °C	Recrystn solvent	Yield, %	-Ir max, cm <sup>-1</sup>	
				νNH	νC=O
1	178–180	Acetone	85	3278	1733
2	162–164	b	70	3260	1734
3	151–153	Ether	60	3300	1735
4	126–127	Ether	60	3260	1728
5	184–188	b	33	3275	1739
6	207–210	Acetone	85	3290	1733
7	198–200	Dioxane	70	3290	1732
8	179–181 <sup>c</sup>	b	50	3288	1732
9	149–150	Acetone	75	3293	1726
10	d	b	91	3340	1733
11	e	Acetone	70	3350	1738

<sup>a</sup> See footnote 7. <sup>b</sup> Analytical material obtained directly from reaction. <sup>c</sup> Phase transition at 170–173°. <sup>d</sup> Very unusual behavior. Decomposition began for this compound at 99° and, before finally liquefying at 185°, it suffered two color changes and gas evolution. <sup>e</sup> Photochemically active, approximate melting range 78–88°.

reagents were the purest grade available from Matheson Coleman and Bell. Solvents were reagent or electronic grade and were dried prior to use.

**Synthesis of Oximes.**—The following procedure is illustrative of the general method used to prepare all oximes with the exception of 4,4'-bis(dimethylamino)benzophenone oxime.<sup>4</sup> A stirred solution of ketone and hydroxylamine hydrochloride (1 equiv each) in pyridine (100 ml) and anhydrous ethanol (200 ml) was heated under reflux for 2 hr. The cooled solutions were concentrated and poured into 600 ml of faintly alkaline (NH<sub>3</sub>) water. The product was collected, washed well with water, dried, and recrystallized to constant melting behavior. In the case of the monosubstituted oximes, two distinct melting ranges were frequently observed. Table I lists the oximes prepared. Since the carbamates prepared from these oximes underwent smooth first-order reaction, isomer separation was not considered necessary. This observation confirms a report<sup>5</sup> that both isomers of substituted benzophenone oximes give the same compound upon treatment with phenyl isocyanate.

**Preparation of Oxime Carbamates.**—The following procedure is illustrative of the general synthesis of compounds 1–17. Tables II and III list the compounds prepared and some of their prop-

erties.<sup>7</sup> Benzophenone oxime (20.0 g, 0.1014 equiv) was dissolved in 50 ml of anhydrous diethyl ether. The solution was stirred magnetically and 12.7 g (0.1068 equiv) of phenyl isocyanate was added dropwise at a rate which maintained a gentle reflux. All glassware had previously been baked dry. After

(4) Prepared by the method of R. D. Morin, J. S. Warner, and R. H. Poirer, *J. Org. Chem.*, **21**, 616 (1956).

(5) O. L. Brady and R. P. Mehta, *J. Chem. Soc.*, **125**, 2297 (1924).

(6) J. Meisenheimer and A. Kuppler, *Justus Liebigs Ann. Chem.*, **539**, 99 (1939).

(7) Satisfactory microanalyses ( $\pm 0.4\%$  for C, H, and N) were reported for all compounds listed in Tables II and III with the following exceptions: Calcd, **11**: C, 66.45; H, 4.38; N, 10.72. Found: C, 66.40; H, 4.62; N, 10.02. Calcd, **13**: C, 87.19; H, 4.57; N, 11.19. Found: C, 87.69; H, 4.81; N, 11.16.

TABLE III  
SYNTHESIS OF BENZOPHENONE OXIME  
2-METHYLPHENYL CARBAMATES<sup>a</sup>

Compd	Mp, °C	Recrystn solvent	Yield, %	—Ir max, cm <sup>-1</sup> —	
				ν <sub>NH</sub>	ν <sub>C=O</sub>
12	127–130	Ether	75	3385	1760
13	122–130	Acetone	43	3380	1758
14	148–152	Acetone	60	3390	1757
15	97–110	Acetone	50	3390	1755
16	127–129	Acetone	73	3380	1757
17	138–140	Acetone	77	3375	1750

<sup>a</sup> See footnote 7.

addition was complete, the mixture was held at reflux for 20 min, cooled, and diluted with 50 ml of ether. The solid was collected on a Buchner funnel, washed with ether, and recrystallized repeatedly from acetone to give 28 g (87.4%) of benzophenone oxime phenylcarbamate. Generally, compounds were repeatedly recrystallized to constant melting behavior.

While ether was a satisfactory solvent for the majority of the syntheses, significant improvement in the yield was obtained when 11 was prepared in benzene and when 13 was made in acetone. In all but two cases, reactions were exothermic and the product began to precipitate shortly after beginning the isocyanate addition. In the cases of compounds 12 and 13, however, catalysis was needed and one drop of triethylamine was used.

A number of the oxime carbamates were readily degraded by light. This was especially true of compound 11, which rapidly darkened even on exposure to an incandescent source. Since all the compounds prepared were thermally unstable, it was not surprising that some analytically pure materials exhibited very wide melting ranges, particularly in the less heat-stable 2-methylphenyl series.

**Kinetics Experiments.**—The reaction system and procedure have previously been described.<sup>1</sup> Initial concentrations were in the range of 0.02–0.03 *M*. Regressions of first-order plots and correlations of the data using the Eyring and Hammett equations were performed by computer.

**Product Isolation and Identification.**—In addition to our previous establishment<sup>1</sup> of the products of reaction, two experiments were performed on the compounds used in this study. A reaction mixture which had been used to determine the rate constant for compound 11 was cooled to room temperature. After it had stood for 3 days, a white solid had separated which was collected, washed, and dried *in vacuo* to give crystals of *p*-nitrophenyldibutylurea, mp 127–129°, identified by peak matching of its ir spectrum with that of an independently synthesized sample of the urea.

*Anal.* Calcd for C<sub>15</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub>: C, 61.42; H, 7.91; N, 14.32. Found: C, 61.21; H, 8.02; N, 14.56.

A second reaction mixture, from a rate determination on compound 12, was concentrated under reduced pressure. Upon cooling to –70°, crystals of benzophenone oxime separated, mp 142–144°. Identification was made by peak matching of the ir spectrum with that of an authentic sample.

**Reversibility of Reaction of 17.**—Dibutylamine (0.490 g, 3.79 mequiv) and 2-methylphenyl isocyanate (0.50 g, 3.76 mequiv) were dissolved in 37 ml of toluene and the solution (total volume 38 ml) was heated at 70° for 1 hr. A 10-ml aliquot of this solution of 2-methylphenyl dibutylurea was added to 100 ml of 2-propanol and titrated with 0.1 *N* aqueous HCl to a bromocresol green end point. The titration required 0.11 ml of HCl solution, indicating a residual amine concentration of  $1.1 \times 10^{-3}$  *M*. The calculated excess of amine was  $0.95 \times 10^{-3}$  *M*.

To a second 10-ml aliquot of the urea solution was added 0.24 g (1.0 mequiv) of 4-dimethylaminobenzophenone oxime. The solution was held at 70° for 10 min and then added to 100 ml of 2-propanol. The quenched solution required 0.50 ml of 0.1 *N* aqueous HCl to reach the bromocresol green end point.

The difference in titrations was 0.39 ml corresponding to an increase in amine concentration of  $3.9 \times 10^{-3}$  *M*. Since the original concentration of urea in the 10-ml aliquot was  $9.74 \times 10^{-2}$  *M*, the increase in dibutylamine concentration corresponded to 4.0% reaction.

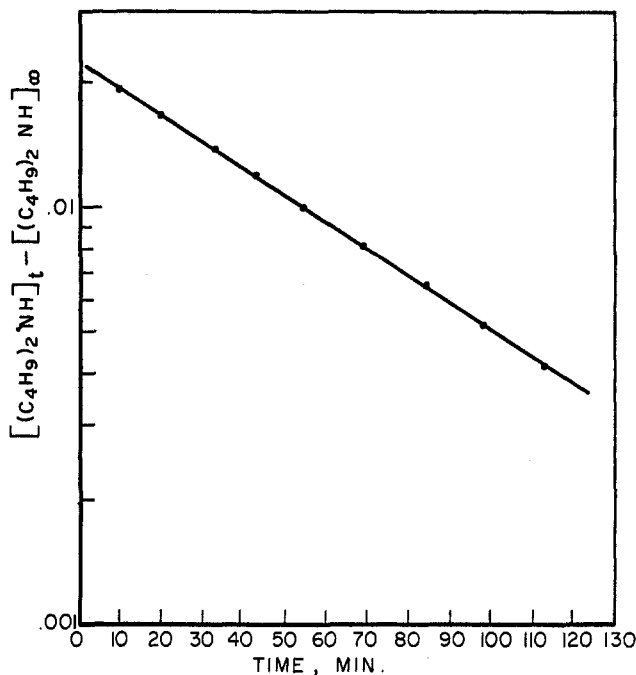


Figure 1.—Reaction of benzophenone oxime phenylcarbamate (1) with dibutylamine at 70.0° and 1/1 reactant ratio.

## Results and Discussion

The oxime carbamates studied react smoothly with dibutylamine, producing the corresponding dibutylureas. In all but one case, the reactions are irreversible and quantitative conversion occurs in from 80 to 1100 min at 70° depending upon substitution. The stoichiometry of the reaction is 1 equiv of amine used per equiv of carbamate reacted. A typical kinetics experiment is presented in Figure 1. Attempts to fit the data to higher order kinetic expressions did not provide straight lines. Since there are two species taking part in the reaction and first-order kinetics are observed, either the carbamate or the amine becomes involved only after the rate-determining step of the reaction. Tables IV and V list first-order rate constants for the compounds studied under a variety of conditions.

**Phenyl Carbamates.**—From the values in Table IV, it is clear that the rate of reaction of 1 with dibutylamine is independent of amine concentration. It is thus the amine which does not participate in the rate-determining step. The overall pathway of reaction, therefore, requires a unimolecular decomposition of the carbamate followed by reaction of the isocyanate thus formed with dibutylamine. The latter reaction is known<sup>8</sup> to be very rapid.

Activation parameters<sup>2</sup> for the reaction of the phenyl carbamates were determined by plotting the appropriate rate constants from Table IV according to the Eyring equation ( $r = 0.999$ ). The calculated value of enthalpy of activation ( $\Delta H^\ddagger$ ) was  $25.7 \pm 0.3$  kcal/mol and the entropy of activation ( $\Delta S^\ddagger$ ) was  $-0.24 \pm 0.39$  cal/deg mol. These values are consistent with a unimolecular rate-determining decomposition<sup>9</sup> and compared quite well with those determined<sup>1</sup> for the similar macromolecular oxime carbamates where  $\Delta H^\ddagger$  was  $24.8 \pm 0.5$  kcal/mol and  $\Delta S^\ddagger$  was  $-1.86 \pm 0.8$  cal/deg

(8) E. H. Dyer, H. A. Taylor, S. J. Mason, and J. Sampson, *J. Amer. Chem. Soc.*, **71**, 4106 (1949).

(9) L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, **1**, 1 (1963).

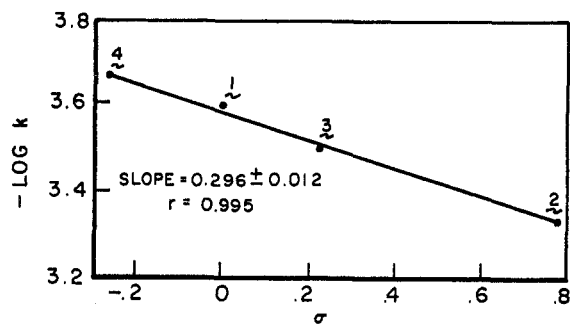


Figure 2.—Reaction of compounds 1–4 with dibutylamine at 70.0° and 1/1 equivalent ratio. Solution of the Hammett equation for position X.

TABLE IV  
FIRST-ORDER RATE CONSTANTS FOR REACTION OF  
BENZOPHENONE OXIME PHENYL CARBAMATES WITH  
DIBUTYLAMINE IN TOLUENE SOLUTION

Compd	Reactant ratio <sup>a</sup>	Temp, °C, ± 0.05	10 <sup>4</sup> k, <sup>b,c</sup> sec <sup>-1</sup>
1	1.0	70	2.507 ± 0.016
1	2.0	70	2.316 ± 0.017
1	5.0	70	2.219 <sup>d</sup>
1	10.0	70	2.740 ± 0.040
1	1.0	80	7.785 ± 0.101
1	1.0	60	0.811 ± 0.001
2	1.0	70	4.323 ± 0.101
3	1.0	70	3.115 ± 0.023
4	1.0	70	2.142 ± 0.001
5	1.0	70	1.058 ± 0.003
6	1.0	70	2.367 ± 0.023
6	1.45	70	2.123 <sup>d</sup>
7	1.0	70	3.347 ± 0.022
8	1.0	70	4.888 ± 0.068
9	1.0	70	11.20 ± 0.10
10	1.0	70	14.59 ± 0.07
11	1.0	70	7.771 ± 0.285

<sup>a</sup> [Amine]<sub>0</sub>/[carbamate]<sub>0</sub>. <sup>b</sup> Average of at least two runs with different initial concentrations. <sup>c</sup> Limits are average deviations of the means. <sup>d</sup> Single experiment.

mol. It thus appeared that the mechanism for both reactions is the same.

The rate constants for the substituted phenyl carbamates were fitted to the Hammett<sup>10</sup> equation. The correlation is shown for position X in Figure 2 and that for position Y in Figure 3. The electronic effect of substituents at position X ( $\rho = +0.296 \pm 0.012$ ) may be interpreted in a manner similar to that used to explain  $\rho$  values for acid-catalyzed ester hydrolyses.<sup>11</sup> For the reaction to proceed, the N–H bond must be broken. This process would be facilitated by an electron-withdrawing substituent, X. However, the pair of electrons forming the N–H bond does not remain localized on the nitrogen atom and instead forms part of the N=C bond in the isocyanate intermediate. The formation of the N=C bond requires nucleophilic displacement to break the existing C–O bond. The nucleophilicity of an electron pair on the nitrogen atom would be increased by an electron-releasing substituent, X. One would thus predict a small absolute value of  $\rho$ . The overall rate acceleration by electron withdrawal at position X suggests that the N–H bond

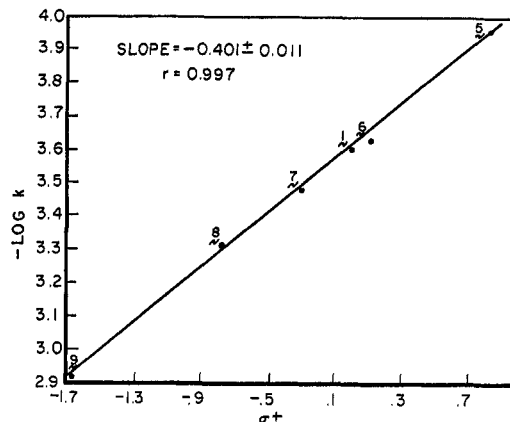


Figure 3.—Reaction of compounds 1 and 5–9 with dibutylamine at 70.0° and 1/1 equivalent ratio. Solution of the Hammett equation for position Y.

breaking is more important in the transition state of the rate-determining step than is the C–O bond breaking.

As in the case of the macromolecular compounds previously reported,<sup>1</sup> the electronic effect at position Y ( $\rho^+ = -0.401 \pm 0.011$ ) indicated involvement of the  $-\text{C}=\text{N}:-$  electrons in the transition state for decomposition. Unlike the macromolecular compounds, however, the rate constants in this case are correlated by  $\sigma^+$  rather than  $\sigma$ . The implication<sup>12</sup> of a  $\sigma^+$  correlation is that a positive charge is generated in the rate-determining transition state. The location of this charge must be one which allows direct conjugation with the substituted aromatic ring. For the most part, reactions correlated by  $\sigma^+$  occur in highly ionizing media and involve carbonium ions where the cationic center is  $\alpha$  to the substituted aromatic ring. There are several exceptions, however, involving thermal reactions in hydrocarbon solvents and free-radical reactions.<sup>13</sup>

**2-Methylphenyl Carbamates.**—The overall similarity between the reactions of the large molecules<sup>1</sup> and the phenyl carbamates seemed to indicate a similar mechanism. The difference in response of the rate constants to the electronic effect of substituents, however, demonstrated that the modes of reaction for the two series of compounds were not identical. The only structural difference in the isocyanate portion of the two series of compounds was that the macromolecular compounds were derived from 2,4-toluenediisocyanate (TDI) rather than phenyl isocyanate. The 4-isocyanate group of TDI is considerably more reactive than is the 2-isocyanate group under the conditions of synthesis.<sup>14</sup> It is thus reasonable to assume that the structure of the macromolecular carbamates is as shown in Chart I; *i.e.*, there is a methyl group adjacent to the carbamate linkage. In order to determine the effect of such substitution, compounds 12–17 were prepared and treated with dibutylamine.

An examination of the rate constants in Table V is revealing. Comparing similarly substituted compounds, *e.g.*, 12 and 1, it is clear that the 2-methylphenyl carbamates react considerably more rapidly

(12) Y. Okamoto and H. C. Brown, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

(13) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 208–209.

(14) M. E. Bailey, V. Kirss, and R. G. Spaunburgh, *Ind. Eng. Chem.*, **48**, 794 (1956).

(10) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(11) E. Tommila and C. N. Hinshelwood, *J. Chem. Soc.*, 1801 (1938).

TABLE V  
FIRST-ORDER RATE CONSTANTS FOR REACTION OF  
BENZOPHENONE OXIME 2-METHYLPHENYL CARBAMATES WITH  
DIBUTYLAMINE IN TOLUENE SOLUTION AT 70.0 AND  
1/1 REACTANT RATIO

Compd	$10^4 k, ^a, ^b \text{ sec}^{-1}$
12	$5.175 \pm 0.057$
13	$1.695 \pm 0.023$
14	$4.689 \pm 0.017$
15	$6.396 \pm 0.039$
16	$6.248 \pm 0.068$
17	$12.29^c \pm 0.14$

<sup>a</sup> Average of two runs with different initial concentrations.  
<sup>b</sup> Limits are average deviations of the means. <sup>c</sup> Initial rates; see text.

than do the phenyl carbamates. This difference, however, is far less for compounds bearing highly electron donating substituents. Correlation of the data in Table V using the Hammett equation shows (Figure 4) that the rate constants follow  $\sigma$  ( $r = 0.979$ ) much more closely than  $\sigma^+$  ( $r = 0.932$ ). The value of  $\rho$  is  $-0.512 \pm 0.034$ . All of the compounds in the 2-methylphenyl series underwent smooth, first-order reaction with dibutylamine with the exception of 17. For this material, there was a decrease in rate constant with time which became noticeable as curvature in the first-order plot after about 60% reaction (10–15 min).

Since behavior of this type can result from reversibility of a reaction, a test of the stability of the product in this reaction was made. 2-Methylphenyldibutylurea was synthesized and allowed to react at 70° with 4-dimethylaminobenzophenone oxime. An increase in the volume of aqueous HCl needed to bring aliquots of this solution, quenched in 2-propanol, to a bromocresol green end point was observed. Equilibrium was apparently reached at approximately 4% reversion to carbamate. Therefore, the rate constant for 17 was taken from the initial points in the first-order plot.

**Mechanistic Implications.**—The change in response of the reaction to electronic effects of substituents on the oxime moiety which attends a change in structure of the isocyanate portion of the molecule is unusual. The fact that all of the compounds studied undergo first-order reactions whose rates are insensitive to amine concentration supports the intramolecular cyclic dissociation as the rate-determining step. It appears that the presence of an ortho methyl group on the isocyanate-derived portion of the molecule changes the manner in which the azomethine group interacts with the carbamate hydrogen atom. That a rate increase is observed when 2-methylphenyl isocyanate is used suggests a steric effect. The similarity of the rate constants for TDI and 2-methylphenyl isocyanate derived carbamates on the one hand and the similarity of activation parameters of the phenyl isocyanate and TDI derived carbamates on the other imply that a single but modifiable mechanism is followed by all of the compounds studied. We originally hypothesized<sup>1</sup> (Chart I) that the dissociation proceeded *via* a concerted, intramolecular transition state. Clearly, this is not possible for all compounds in view of the substituent effects. The intramolecular nature of the transition state is, however, required by the gross effect that the rate in all cases is favored by an electron-donating substituent Y. The possibility, then, that the reaction is not always concerted presents itself.

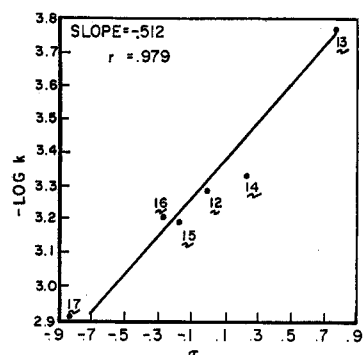


Figure 4.—Reaction of compounds 12–17 with dibutylamine at 70.0° and 1/1 equivalent ratio. Solution of the Hammett equation.

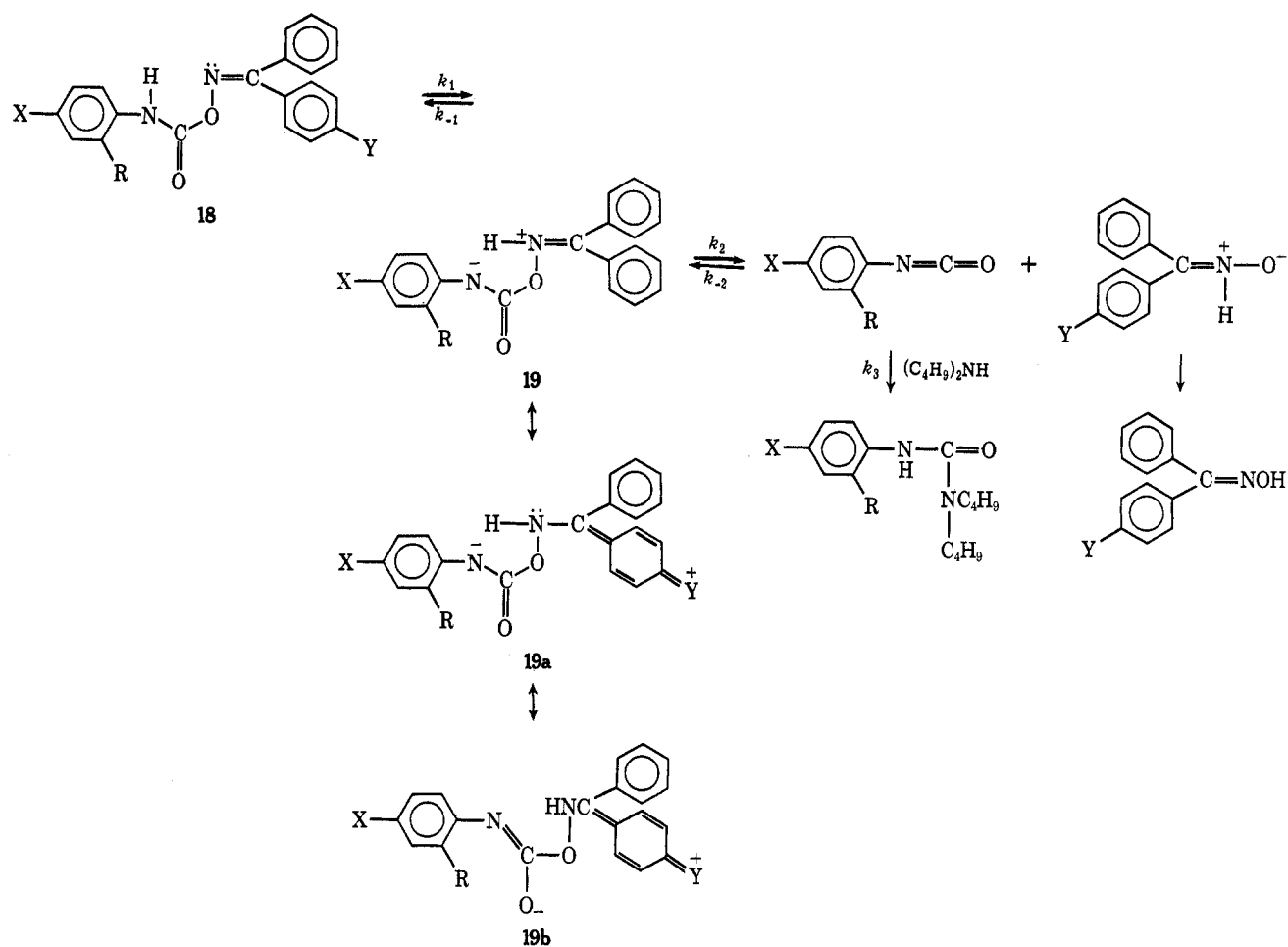
From the positive value of  $\rho_x$ , the implication may be drawn that proton transfer in the rate-determining transition state is more important than C–O bond cleavage. If these processes are formally separated, then the scheme shown in Chart IV results. The generalized compound 18 may intramolecularly transfer its carbamate proton, producing the zwitterion 19. If 19 has a finite lifetime, then the positive center may enter into resonance with the substituent Y. Structure 19a is one canonical form of such an interaction. One might expect that if the lifetime of 19 is sufficient to obtain  $\sigma^+$  correlation at position Y then the effect of substituent X should be correlated by  $\sigma^-$ . The center of negative charge in 19, however, is cross-conjugated and stabilization in the manner of structure 19b is possible and may be energetically preferable to extended overlap with X in view of the resulting loss in rotational freedom of the aromatic nucleus. Under conditions where the lifetime of 19 is very short or nonexistent, the transformation becomes concerted and the involvement of substituent Y takes the form of inductive effects only and correlation with  $\sigma$  would be observed.

For the overall process to follow first-order kinetics,  $k_3$  must be greater than either  $k_2$  or  $k_1$ . The high reactivity of dibutylamine for isocyanates easily satisfies this requirement. The ratio of  $k_1$  to  $k_2$  will then determine whether  $\sigma$  or  $\sigma^+$  best correlates the effect of substituent Y. When  $k_2$  is smaller than  $k_1$ , as appears to be the case for R = H, 19 may be sufficiently long-lived to be resonance stabilized. When  $k_2$  is increased so that it becomes larger than  $k_1$ , as due to the steric interaction when R = CH<sub>3</sub>, then 19 does not intervene as an intermediate in the reaction and correlation with  $\sigma$  is observed.

The absolute value of  $\rho_y$  is quite small for a reaction which follows  $\sigma^+$ . This may be due to the orthogonality of the azomethine lone pair and the  $\pi$ -electron system of the benzophenone oxime moiety which obviates direct resonance interaction with Y. Only after the azomethine double bond electrons begin to effect charge delocalization can the ring electrons become involved. In effect, then, Y does not stabilize the primary positive charge but only the charge induced at the azomethine carbon atom. Thus, while  $\sigma^+$  correlation is observed, the magnitude of stabilization is much lower than, for example, that found<sup>15</sup> for substituted benzylic cations, and the value of  $\rho$  is correspondingly small.

(15) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Amer. Chem. Soc.*, **77**, 3044 (1955).

CHART IV



The small value of  $\rho$  thus argues against an alternative mechanism to that presented in Chart IV wherein proton transfer is to the azomethine double bond electrons. Such an alternative is also unlikely in that it would lead most reasonably to a product derived from a phenylarylnitrosomethane. Such products have not been detected in the reaction mixtures, whereas oximes have been isolated.

#### Conclusion

It appears that benzophenone oxime carbamates dissociate *via* a five-center intramolecular transition state to oximes and isocyanates. The pathway is supported by the kinetic order of the reaction, activation parameters, and the overall substituent effect. Depending upon the degree of steric crowding in the transition

state, the decomposition may be synchronous. In the case of uncrowded molecules, a zwitterionic intermediate is detectable using Hammett equation correlations. The nature of the transition state is such that steric crowding may be introduced at a location far removed from the seat of positive charge. The net effect thus appears to be a steric effect on the electronic effect of substituents 11 bonds removed from the bulky substituent.

**Registry No.**—1, 25151-09-1; 2, 34804-53-0; 3, 34804-54-1; 4, 34804-55-2; 5, 34792-32-0; 6, 34804-56-3; 7, 34804-57-4; 8, 34804-58-5; 9, 34792-33-1; 10, 34804-59-6; 11, 34804-60-9; 12, 34804-61-0; 13, 34804-62-1; 14, 34804-63-2; 15, 34804-64-3; 16, 34804-65-4; 17, 34804-66-5; dibutylamine, 111-92-2.