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REACTIONS OF ARYLCARBAMOYL CHLORIDES–I

THE SPONTANEOUS FORMATION OF ARYL ISOCYANATES

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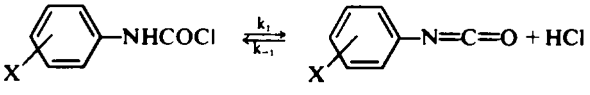
Abstract—Equilibrium and rate constants of formation of isocyanates from arylcarbamoyl chlorides have been measured in acetonitrile. Electronic effects upon the rate constants are very small, but the equilibrium constants follow the Hammett equation, using σ^-, and $\rho = -0\cdot52$, and *ortho* Me groups increase the equilibrium constant. These results suggest a concerted, and possibly four center, mechanism of elimination of HCl.

The elimination of hydrogen chloride from N-arylcarbamoyl chlorides (**1**) to give aryl isocyanates (**2**) is an important reaction; although to date there is no extensive study of its mechanism.

The equilibria have been examined qualitatively[1,2] for a limited number of arylcarbamoyl chlorides (X = H, halogen) in some nonpolar aprotic solvents, and the reaction rates[1,3] have been measured in the presence of excess triethylamine, using infrared spectroscopy, titrimetry of developed hydrogen chloride, or gravimetry to follow the reaction. In the present work we have examined the equilibria and the rates of the spontaneous reaction in acetonitrile by UV spectroscopy with low reactant concentrations, for several aryl carbamoyl chlorides and determined the electronic and steric effects upon the rate and equilibrium constants. In a following paper we discuss the amine catalysis of these reactions.



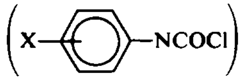
1 **2**

EXPERIMENTAL

Materials. Acetonitrile was purified by the method of Coetzee.[4] The aryl isocyanates were commercial samples or were synthesized from the aniline and phosgene.[5] They were freshly distilled under reduced pressure before use. The carbamoyl chlorides were prepared from the isocyanate and HCl (or DCl) in hexane,[6] in yields > 75%. (Their m.ps are given in Table 1). They were analyzed by hydrolysis in standard NaOH followed by back titration, and because of their instability freshly prepared and analyzed samples were always used.

Equilibria. The equilibrium constants were determined by adding an equilibriated soln of the carbamoyl chloride at 23·5° in MeCN to N,N-dimethylaniline or its *p*-bromo derivative in MeCN. There is immediate reaction between the amine and HCl, which is followed by a slow decomposition of the carbamoyl chloride. The decreasing absorbance of the aromatic amine was followed with time and the difference between the initial absorbance of the amine and that extrapolated back to zero time after addi-

Table 1. Arylcarbamoyl chloride



X	m.p.
4-PhCH$_2$O	96–97°
4-MeO	64–65°
4-EtO	81·5–82·5°
4-Me	86·5–87·5°
3-Me	57–58·5°
H	45–46° (45°[a])
3-MeO	65·5–67° (67–68°[c])
4-Cl	122–123°[b]
3-Cl	91–92° (95–96°[c])
3-NO$_2$	111–112°
4-NO$_2$	147–148°
2,6-Me$_2$	76–77°

[a] Ref 6.

[b] This compound has been reported, Refs 1, 3, but no m.p. has been given.

[c] ND compound.

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tion of the carbamoyl chloride gave the concentration of HCl in equilibrium with **1** and **2**. The absorbances were measured using a Gilford spectrophotometer, in the range 290–320 nm depending upon the amine. A range of substrate concentrations from 10^{-2} to 4×10^{-2} M was used in these determinations, and a large number of independent determinations were made (Table 2). The deviations are calculated as $0{\cdot}675[\Sigma x_i^2 - n\bar{x}^2/n(n-1)]^{1/2}$, where n is the number of experiments, x_i is a calculated value of K and $\bar{x}$ is the arithmetical mean.

The equilibrium constants for deuterated compounds and the isotopic purity of these compounds were determined using a Perkin Elmer 337 IR spectrometer, at the frequencies of 3270, and 2350 cm^{-1} for the NH and ND stretch and 2240 cm^{-1} for the asymmetric isocyanate stretch.

Kinetics. The rates of spontaneous elimination of HCl from the carbamoyl chlorides in MeCN were measured conductimetrically at 23·5°. For $0{\cdot}3\times10^{-3}$ M to 3×10^{-3} M HCl in MeCN conductivity varies linearly with concentrations, c.f. Ref 4. For this range of concentrations we observed the relation

$$\Lambda = 0{\cdot}183 + 1{\cdot}589\,[\mathrm{HCl}].$$

The rate constants k_1 and k_{-1} for the forward and back reactions were calculated using Eqs (1)[7] and (2)

$$k_1 = \frac{K}{(K+2\beta)\,.\,t}\ln\frac{U_t-(K+2\beta)}{U_0-(K+2\beta)}\cdot\frac{U_0}{U_t} \qquad (1)$$

$$k_1/k_{-1} = K \qquad (2)$$

where U_0 is the difference between [HCl] at time 0 and its equilibrium value, β, and U_t is the difference between [HCl] at time t and its equilibrium value, β.

RESULTS AND DISCUSSION

Structural effects upon the equilibria. Electron attracting groups decrease the equilibrium constants, K, (Table 2), and for *meta* and *para* substituents there is a linear free energy relationship between σ^- and log K[8] following Eq 3.

$$\log K = -2{\cdot}17 - 0{\cdot}52\,\sigma^- \qquad (3)$$

This correlation of log K with σ^- (Fig 1) suggests that mesomeric effects are controlling the equilibrium, but the relatively small value of $\rho = -0{\cdot}52$ shows that these effects are not large.

As expected steric effects increase the equilibrium constant for formation of the isocyanate as

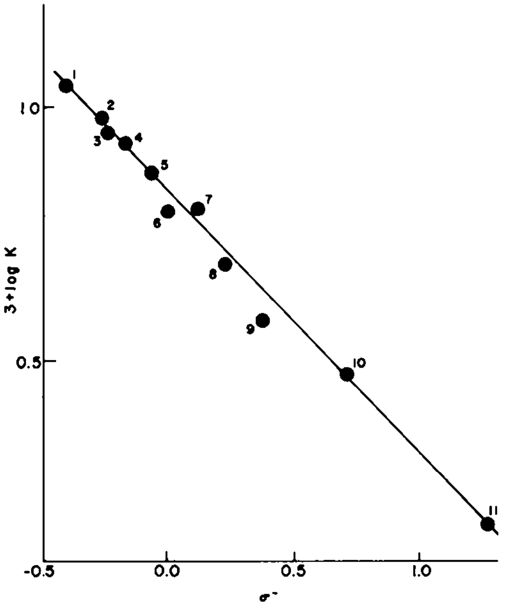
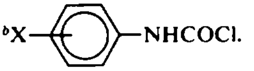


Fig 1. Relation between log K and σ^- in acetonitrile at 23·5°. The compounds are listed in Table 2.

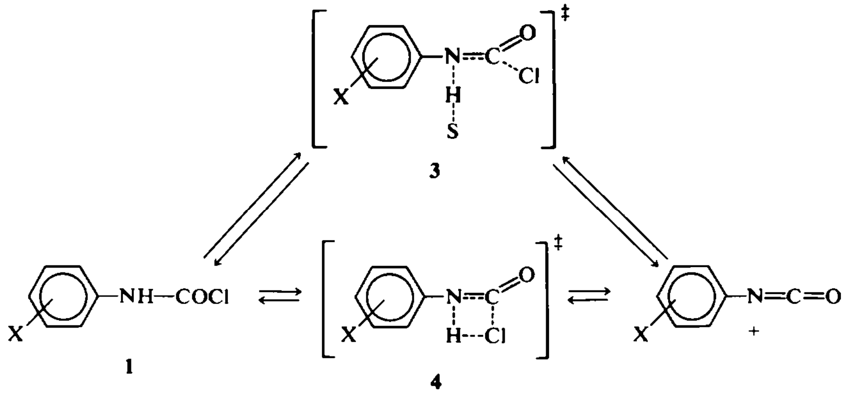
Table 2. Equilibrium and rate constants for conversion of carbamoyl chlorides into isocyanates[a]

Rn. No.	X[b]	No. of independent determinations	10^3 K mole l.$^{-1}$	10^4 k_1, sec^{-1}	10^2 k_{-1}, l. mole^{-1} sec^{-1}
1	4-PhCH$_2$O	14	11·1 ± 0·40		
2	4-MeO	16	9·61 ± 0·31	2·37 ± 0·10	2·47
3	4-EtO	20	8·96 ± 0·24		
4	4-Me	18	8·54 ± 0·19	2·55 ± 0·15	2·98
5	3-Me	18	7·47 ± 0·21		
6	H	17	6·26 ± 0·21		
7	3-MeO	14	6·48 ± 0·13		
8	4-Cl	14	4·90 ± 0·16		
9	3-Cl	18	3·79 ± 0·16	2·35 ± 0·17	6·19
10	3-NO$_2$	11[c]	2·96 ± 0·10	2·65 ± 0·15	8·95
11	4-NO$_2$	9	1·49 ± 0·05		
12	2,6-Et$_2$	12[c]	573 ± 8·4	24·4 ± 1·6	0·043

[a] At 25·0° in MeCN, N,N-dimethylaniline was the base in the determinations of K unless specified.

[b] 

[c] N,N-dimethyl *p*-bromoaniline was used as the base.



shown by the value of K for the 2,6-diethyl compound (Table 2).

The structural deuterium isotope effect $K_H/K_D = 3{\cdot}8$ for 3-chlorophenylcarbamoyl chloride is close to the value of 3·6 calculated using the N–H stretching and bending frequencies and the H–Cl stretching frequency.[9] (The stretching frequencies for HCl and DCl are from Ref 10). However, this agreement may be fortuitous because the calculation makes no allowance for the contribution of the rotational levels of HCl and DCl, and the agreement is much less satisfactory for 4-methoxy phenyl carbamoyl chloride where $K_H/K_D = 2{\cdot}1$.

Structural effects upon reaction rates. The first order rate constants, k_1, for elimination of HCl from the carbamoyl chlorides are almost independent of the electronic effects of substituents (Table 2), suggesting that there is little charge development in the transition state, so that we exclude mechanisms which involve extensive proton transfer in the transition state. Transition states **3** or **4** fit these observations, although the latter seems more probable in view of the low basicity of acetonitrile. The electronic effects upon k_{-1} suggest that formation of the C–Cl bond is ahead of formation of the C–H bond.

There is considerable steric hindrance to the addition of HCl by 2,6-diethyl groups, which also sterically accelerate the elimination of HCl from the carbamoyl chloride, and markedly increase the equilibrium constant K. These observations suggest that there is a marked change in the geometry and hybridization of the nitrogen atom in the transition state.

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