**3-Methyl-3-buten-2-*d*-2-ol.** 3-Methyl-3-buten-2-one was reduced with lithium aluminum deuteride in ether to the carbinol in 35% yield.

***trans*-1-Bromo-4-methyl-4-hexene-5-*d*.** Ethyl *trans*-4-methyl-4-hexen-5-*d*-oate was prepared from 3-methyl-3-buten-2-*d*-2-ol and ethyl orthoacetate in 72% yield by the method of Johnson et al.[16] Reduction of the ester with lithium aluminum hydride followed by the reaction of the carbinol with phosphorus tribromide in pyridine at low temperature[17] gave the title compound.

***trans*-1-Aryl-5-methyl-5-hepten-1-ols.** The title compounds were prepared from the Grignard reagent of the corresponding *trans*-4-methyl-4-hexen-1-yl bromide and arylmethanals in 11–55% yields. A typical preparation is described.

To 480 mg (0.02 g-atom) of magnesium shavings covered with anhydrous ether was added a crystal of iodine followed by 3.54 g (0.02 mol) of *trans*-1-bromo-4-methyl-4-hexene in 20 mL of anhydrous ether. The addition was carried out with stirring and at room temperature. Stirring was continued until complete disappearance of magnesium (about 90 min). Benzaldehyde (2.12 g, 0.02 mol) in 15 mL of anhydrous ether was then added dropwise to the reaction mixture under stirring and cooling with ice and water. The stirring was continued for 2 h followed by addition of an ice-cold saturated aqueous solution of ammonium chloride. The product was then extracted from the reaction mixture several times with ether, the combined extracts were washed with water and dried over magnesium sulfate, the ether was evaporated, and the residue was distilled under reduced pressure. It was necessary to purify the product by high-pressure LC using a Porasil column and chloroform as the mobile phase. The yield was 1.81 g (44.3%).

***trans*-1-Chloro-1-aryl-5-methyl-5-heptenes.** A typical preparation is described. To a mixture of *trans*-1-phenyl-5-methyl-5-hepten-1-ol (408 mg, 2 mmol), anhydrous pyridine (0.194 mL), and anhydrous ether (5 mL) at −20 °C was added 0.176 mL (2.4 mmol) of freshly distilled thionyl chloride dropwise and with stirring. Stirring was continued at −15 to −20 °C for 45 min and the reaction mixture brought to room temperature. Pyridinium hydrochloride was then filtered off and the solvent and unreacted reagents removed in vacuo. Despite these precautions, the chlorides contained 10–30% of the elimination product. Further purification proved to be unnecessary since the solvolysis rates were found to be independent of the contamination.

**Acknowledgment.** This work was supported by the Research Council of Croatia and Grant No. 02-011-1 (P-L-480) administered by National Institutes of Health.

**Registry No.** 1-*1*-*d* (Y = *p*-OCH$_3$), 71434-98-5; 1-*1*-*d* (Y = *p*-CH$_3$), 71434-99-6; 1-*1*-*d* (Y = H), 71435-00-2; 1-*1*-*d* (Y = *p*-Br), 71435-01-3; 1-*1*-*d* (Y = *m*-Br), 71435-02-4; 1-*2,2*-$d_2$ (Y = *p*-OCH$_3$), 71435-03-5; 1-*2,2*-$d_2$ (Y = *p*-CH$_3$), 71435-04-6; 1-*2,2*-$d_2$ (Y = H), 71435-05-7; 1-*2,2*-$d_2$ (Y = *p*-Br), 71435-06-8; 1-*2,2*-$d_2$ (Y = *m*-Br), 71435-07-9; 1-*6*-*d* (Y = *p*-OCH$_3$), 71435-08-0; 1-*6*-*d* (Y = *p*-CH$_3$), 71435-09-1; 1-*6*-*d* (Y = H), 71435-10-4; 1-*6*-*d* (Y = *p*-Br), 71435-11-5; 1-*6*-*d* (Y = *m*-Br), 71435-12-6; 1-(*p*-methoxyphenyl)-1-*d*-methanal, 19486-71-6; 1-(*p*-methylphenyl)-1-*d*-methanal, 13277-99-1; 1-phenyl-1-*d*-methanal, 3592-47-0; 1-(*p*-bromophenyl)-1-*d*-methanal, 42007-03-4; phenyl)-1-*d*-methanal, 71435-13-7; (*trans*)-1-bromo-4-methyl-4-hexene-*1,1*-$d_2$, 71435-14-8; ethyl (*trans*)-4-methyl-4-hexenoate, 58203-62-6; 3-methyl-3-buten-2-ol-2-*d*, 71435-15-9; 3-methyl-3-buten-2-one, 814-78-8; (*trans*)-1-bromo-4-methyl-4-hexene-*5*-*d*, 71435-16-0; ethyl *trans*-4-methyl-4-hexenoate-5-*d*, 71435-17-1; ethyl orthoacetate, 78-39-7; (*trans*)-1-(*p*-methoxyphenyl)-5-methyl-5-hepten-1-ol, 71435-18-2; (*trans*)-1-(*p*-methylphenyl)-5-methyl-5-hepten-1-ol, 71435-19-3; (*trans*)-1-phenyl-5-methyl-5-hepten-1-ol, 71435-20-6; (*trans*)-1-(*p*-bromophenyl)-5-methyl-5-hepten-1-ol, 71435-21-7; (*trans*)-1-(*m*-bromophenyl)-5-methyl-5-hepten-1-ol, 71435-22-8; (*trans*)-4-methyl-4-hexen-1-yl bromide, 71435-23-9; (*trans*)-1-chloro-1-(*p*-methoxyphenyl)-5-methyl-5-heptene, 56040-03-0; (*trans*)-1-chloro-1-(*p*-methylphenyl)-5-methyl-5-heptene, 56040-04-1; (*trans*)-1-chloro-1-phenyl-5-methyl-5-heptene, 56040-05-2; (*trans*)-1-chloro-1-(*p*-bromophenyl)-5-methyl-5-heptene, 56040-06-3; (*trans*)-1-chloro-1-(*m*-bromophenyl)-5-methyl-5-heptene, 56112-25-5.

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# Buffer Catalysis in the Hydrolysis of Picryl Chloride[1]

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The kinetics of the hydrolysis of picryl chloride were studied between pH 7.06 and 11.60 with different buffers at various concentrations. The reaction is strongly catalyzed by tertiary amines (*N*-ethylmorpholine, 2,4,6-trimethylpyridine, and Dabco) and also by carbonate and bicarbonate. A small increase in rate is also observed with phosphate trianion and borate. The catalysis seems to be of the nucleophilic type for *N*-ethylmorpholine, 2,4,6-trimethylpyridine, carbonate, and bicarbonate, but a mechanism involving general base-catalyzed addition of water is suggested for the other bases.

The mechanism of aromatic nucleophilic substitution of activated substrates has been extensively studied during the last 10 years.[2] Amines are probably the most studied nucleophiles and kinetic studies of their intra- or intermolecular reactions greatly contributed in firmly establishing the multistep nature of the mechanism.[3] In general terms, it can be described by Scheme I, where NuH represents any neutral nucleophile. In this scheme all the reaction paths identified at present are shown, but not all of them take place simultaneously. With many amines as nucleophiles the product-forming steps are rate determining, and general base catalysis through the I → II → IV → V pathway is observed. Specific base catalysis attributed to the pathway I → III → IV → V was reported in the reaction of imidazole with 2,4-dinitrofluorobenzene.[4] General base catalyzed addition of water to 4,6-dinitrobenzofuroxan,[5] which corresponds to the diagonal pathway I → IV in Scheme I, is the only known example where the formation of a Meisenheimer complex is general base catalyzed.

One reason why base catalysis of the addition step is not usually found could be that, under the conditions of the

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(1) Presented in part in the 1st Conference on Physical Chemistry, Sept 1978, La Plata, Argentina.

(2) For recent reviews on nucleophilic aromatic substitution see: (a) C. F. Bernasconi, *MTP Int. Rev. Sci.: Org. Chem., Ser. One*, **3**, 33 (1973); (b) F. Pietra, *Q. Rev., Chem. Soc.*, **23**, 504 (1969).

(3) C. F. Bernasconi, C. L. Gehriger, and R. H. de Rossi, *J. Am. Chem. Soc.*, **98**, 8451 (1976); C. F. Bernasconi, R. H. de Rossi, and P. Schmid, *J. Am. Chem. Soc.*, **99**, 4090 (1977).

(4) R. H. de Rossi, A. B. Pierini, and R. A. Rossi, *J. Org. Chem.*, **43**, 2982 (1978).

(5) F. Terrier, F. Millot, and W. P. Norris, *J. Am. Chem. Soc.*, **98**, 5883 (1976).

Scheme I

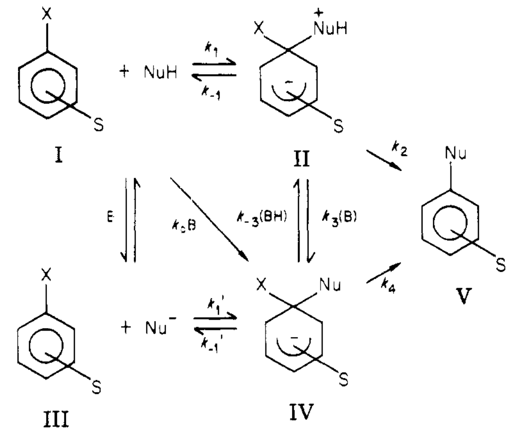


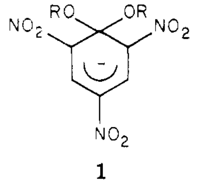
Table I. Rate Constants for the Hydrolysis of Picryl Chloride in Water at 25 °C[a]

| pH | $10^4 k_o$,[b] $s^{-1}$ | $10^4 k_{B_t}$,[c] $M^{-1} s^{-1}$ | pH | $10 k_o$,[b] $s^{-1}$ | $10^4$-$k_{B_t}$,[c] $M^{-1} s^{-1}$ |
|---|---|---|---|---|---|
| 7.06[d] | 0.006 97 | 2.64 | 10.05[g] | 0.840 | [j] |
| 8.21[e] | 0.0104 | 0.151 | 10.20[h] | 1.34 | 18.8 |
| 8.21[e,f] | 0.009 25 | 0.136 | 10.20[g] | 1.25 | [j] |
| 8.48[g] | 0.0252 | 0.0328 | 10.30[i] | 1.61 | 4.08 |
| 8.60[g] | 0.0341 | 0.0382 | 10.41[i] | 1.78 | 4.58 |
| 8.90[h] | 0.0722 | 4.48 | 10.70[i] | 3.26 | 2.70 |
| 9.03[i] | 0.0888 | 0.188 | 10.71[h] | 3.05 | 21.7 |
| 9.10[g] | 0.0902 | 0.127 | 11.00[i] | 7.95 | 12.4 |
| 9.22[e] | 0.122 | 0.616 | 11.30[i] | 14.7 | 22.7 |
| 9.49[g] | 0.251 | 0.282 | 11.40[i] | 20.5 | 22.2 |
| 9.50[g] | 0.287 | 0.917 | 11.60[i] | 39.4 | 33.3 |
| 9.54[h] | 0.320 | 10.7 | | | |

[a] $\mu = 1$ M (NaCl), solvent contains 2% dioxane. [b] $k_o = k_{OH}[OH]$ of eq 1. [c] $k_{B_t}$ is the slope of $k_{obsd}$ vs. total buffer concentration (0.02–0.20 M). [d] *N*-Ethylmorpholine buffer. [e] Dabco buffer. [f] $NaNO_3$ as compensating electrolyte. [g] Borax buffer. [h] Carbonate buffer. [i] Phosphate buffer. [j] Not detected experimentally.

experiments, the energies of states II and III are very different, making the pathway I → II → IV or I → III → IV the preferred reaction path.[6] We think that water is a neutral nucleophile which under the proper conditions could add to the aromatic nucleus through the I → IV pathway. In the hydrolysis of aromatic substrates, concerted catalysis of water addition is not detected because under the conditions where most experiments are carried out (usually high pH) the pathway I → III → IV is certainly the lowest energy path.

Since it has been shown that leaving-group departure from Meisenheimer complexes like 1 is general acid cata-



1

lyzed,[7] the addition of an alcohol to the aromatic ring, the microscopic reverse, should be general base catalyzed, and the same should be true for water addition.

To observe base catalysis in the hydrolysis, one should have to be able to work at low pH, otherwise the HO⁻ reaction would be overwhelming. Since picryl chloride (2) has a relatively high reactivity and a good leaving group, thus making the formation of the intermediate rate determining, we chose this substrate for our study.

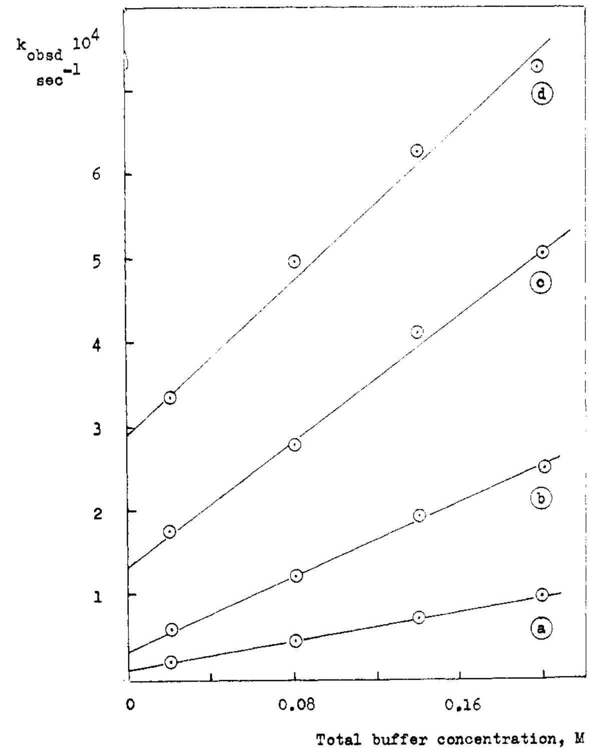


**Figure 1.** Effect of buffer concentration and pH on $k_{obsd}$ for the hydrolysis of picryl chloride (carbonate buffer, 25 °C, $\mu = 1$ M): (a) pH = 8.9, (b) pH = 9.54, (c) pH = 10.20, (d) pH = 10.71.

Table II. Rate Constant for Catalysis by Buffer Species[a]

| base | p$K_a$[b] | $10^3 k_B$, $M^{-1} s^{-1}$ | base | p$K_a$[b] | $10^3 k_B$, $M^{-1} s^{-1}$ |
|---|---|---|---|---|---|
| $H_2O$ | −1.74 | 1.16 $10^{-6}$ [c] | borate | 8.9[d] | 0.02 |
| | | | Dabco | 9.2[d] | 0.117 |
| $CO_3H^-$ | 7.33 | 0.144 | $CO_3^{2-}$ | 9.7[e] | 2.39 |
| 2,4,6-trimethylpyridine | 7.59 | 4.3 | $PO_4^{3-}$ | 12.32[f] | 8.52 |
| | | | $HO^-$ | 15.7[g] | 732 |
| *N*-ethylmorpholine | 8.03 | 2.7 | | | |

[a] $\mu = 1$ M, temperature 25 °C. [b] p$K_a$ at $\mu = 1$ M unless otherwise quoted. [c] Obtained from $k_B^{H_2O}/55.5$: J. Murto, *Acta Chem. Scand.*, **20**, 310 (1966). [d] J. M. Sayer and W. P. Jencks, *J. Am. Chem. Soc.*, **91**, 6353 (1969). [e] W. P. Jencks and M. Gilchrist, *ibid.*, **90**, 2622 (1968). [f] Thermodynamic value: J. H. Butler, "Ionic Equilibrium, A Mathematical Approach", Addison-Wesley, Reading, MA, 1964 p 209. [g] J. M. Sayer and W. P. Jencks, *J. Am. Chem. Soc.*, **95**, 5637 (1973).

## Results

In aqueous solution picryl chloride hydrolyzes to picrate anion [$\lambda_{max}$ = 358 nm ($\epsilon$ 15 000)]. The observed pseudo-first-order rate constant $k_{obsd}$ increases with the pH and the concentration of buffer at constant ionic strength ($\mu$ = 1 M, NaCl as compensating electrolyte; Table I). In all cases but one (see below) the UV–visible spectrum of the final solution is identical with that of picrate anion under similar conditions. In the spectrum recorded at several reaction times a good isosbestic point is found.

The slopes of the plots of $k_{obsd}$ vs. total buffer concentration increase with increasing pH (Figure 1), indicating that it is the base constituent of the buffer which catalyzes the reaction. The plot of the slopes of Figure 1 vs. the fraction of free base gives a measurable intercept which

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(6) W. P. Jencks, *Chem. Rev.*, **72**, 705 (1972).

(7) C. F. Bernasconi, *Acc. Chem. Res.*, **11**, 147 (1978); C. F. Bernasconi and J. R. Gandler, *J. Am. Chem. Soc.*, **100**, 8117 (1978).

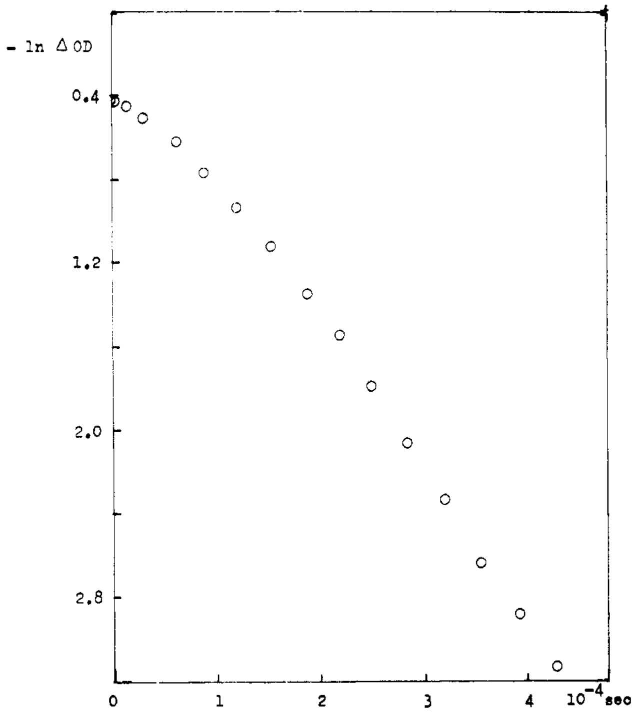


**Figure 2.** Representative plot of ln ΔOD vs. time for the hydrolysis of **2** with 2,4,6-trimethylpyridine buffer at 25 °C, $\mu$ = 1 M, pH = 7.98, $[\mathbf{2}]_0 = 5.1 \times 10^{-5}$ M, and $[\text{buffer}]_0$ = 0.1 M.

we interpreted as the rate coefficient for catalysis by $HCO_3^-$ (Table II). With all the other buffers the intercepts of similar plots are zero within experimental error. Thus $k_{obsd}$ can be represented by eq 1 where $[OH^-]$ is defined as

$$k_{obsd} = k_{OH}[OH^-] + k_B[B] \quad (1)$$

$10^{-(14-pH)}$. The plot (not shown) of the intercepts of the buffer plots vs. $[OH^-]$ gives a straight line with slope 0.732 $M^{-1}\ s^{-1}$, in good agreement with literature values.[8] The intercept of this plot is indistinguishable from zero.

The increase in $k_{obsd}$ with buffer concentration is significant in the case of carbonate, bicarbonate, Dabco (1,4-diazabicyclo[2.2.2]octane) and 2,4,6-trimethylpyridine but is only about 10–30% in the case of phosphate and borate. With 2,4,6-trimethylpyridine as buffer the plots of ln ΔOD vs. time are linear only after 10–20% reaction (Figure 2 is representative). In repetitive recording of the spectrum of the reaction solution we could not detect the formation of any intermediate. This result can be explained by eq 2.

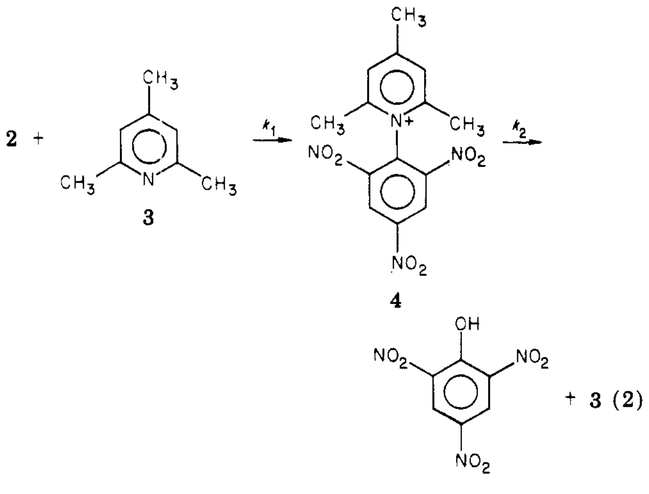


Table III. Effect of the Addition of $Na_2SO_4$ on the Rate of Hydrolysis of Picryl Chloride at 25 °C[a]

| $[Na_2SO_4]$, M | $10^3 k_{obsd}$, $s^{-1}$ | $[Na_2SO_4]$, M | $10^3 k_{obsd}$, $s^{-1}$ |
|---|---|---|---|
| 0.02 | 3.10 ± 0.05 | 0.14 | 3.17 ± 0.05 |
| 0.08 | 3.07 ± 0.09 | 0.20 | 3.14 ± 0.03 |

[a] $\mu$ = 1 M (NaCl), pH = 11.62, $[\mathbf{2}]_0 = 4.6\ 10^{-5}$ M.

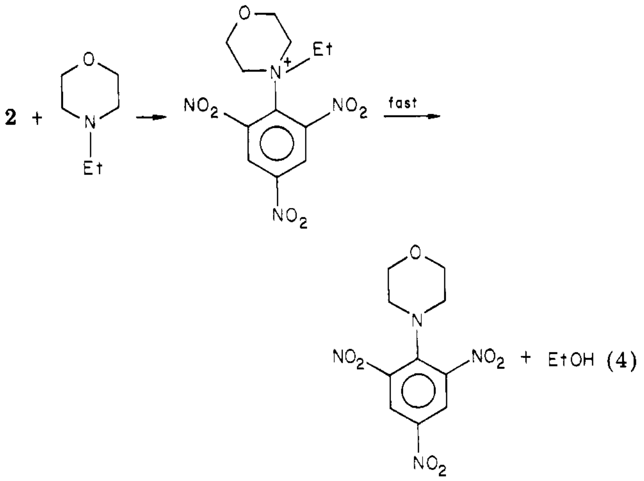
Since the spectrum of the *N*-picryl-2,4,6-pyridinium ion **4** is expected to be quite similar to that of picryl chloride, the formation of **4** is not detected spectroscopially in the range of wavelength useful for examination (above 280 nm).

The change in optical density with time for the reaction described in eq 2 is given by eq 3,[9] were $k_1'$ is the pseudo-

$$\frac{OD_\infty - OD}{OD_\infty} = \frac{k_2}{k_2 - k_1'}e^{-k_1't} - \frac{k_1'}{k_2 - k_1'}e^{-k_2t} \quad (3)$$

first-order rate constant for the reaction of 2,4,6-trimethylpyridine with picryl chloride, i.e., $k_1[\mathbf{3}]_0$. We could fit our data to eq 3 using $k_1 = 4.3\ .10^{-3}\ M^{-1}\ s^{-1}$ and $k_2 = 7.10^{-5}\ s^{-1}$.

*N*-Ethylmorpholine also catalyzes the reaction very strongly, but the product formed is not picric acid in this case, but mostly *N*-picrylmorpholine. This result can be explained by eq 4.



Other tertiary amines are known to react in this way with activated aromatic substrates.[10]

Since the increase in rate with phosphate and borate buffers is very small, the possibility that the catalytic effect is due to a specific salt effect has to be considered.[11] The effect of salts in the hydrolysis of 2,4-dinitrofluorobenzene has been studied,[12] and it was reported that anions of low charge density have the highest positive salt effect; thus we investigated the effect of the change of concentration of an electrolyte of low charge density on the rate of hydrolysis of picryl chloride using $Na_2SO_4$ in a concentration range similar to that of the buffer (0.02–0.20 M). In this case $k_{obsd}$ is constant within experimental error, and there is no trend in the rate to increase with increasing sulfate concentration (Table III). Although this result does not prove that the small catalytic effect observed with borate

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[8] J. Murto, *Acta Chem. Scand.*, **20**, 310 (1966).

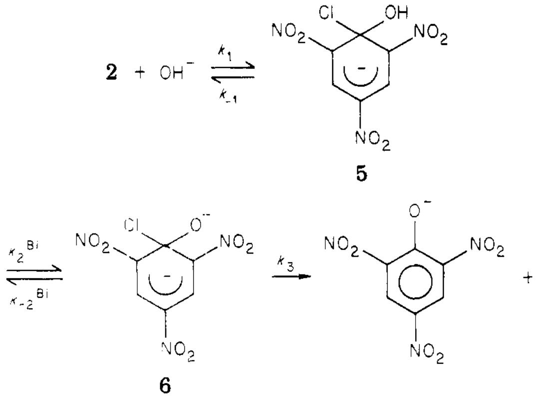
[9] R. E. Weston, Jr., and H. A. Schwarz, "Chemical Kinetics", Prentice-Hall, Englewood Cliffs, NJ, 1972, p 17.

[10] (a) H. Leymann, *Ber. Dtsch. Chem. Ges.*, **15**, 1234 (1882); (b) T. M. Ivanova and S. M. Shein, *J. Org. Chem., USSR* (*Engl. Transl.*), **14**, 536 (1978).

[11] P. Salomaa, A. Kankaanpera, and M. Lahti, *J. Am. Chem. Soc.*, **93**, 2084 (1971).

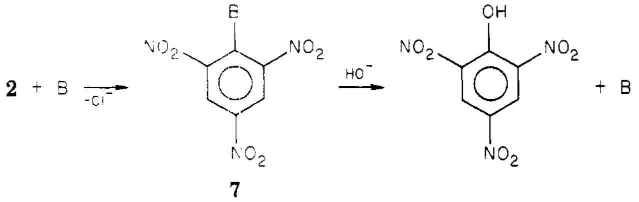
[12] C. A. Bunton and L. Robinson, *J. Am. Chem. Soc.*, **90**, 5965 (1968).

Scheme II

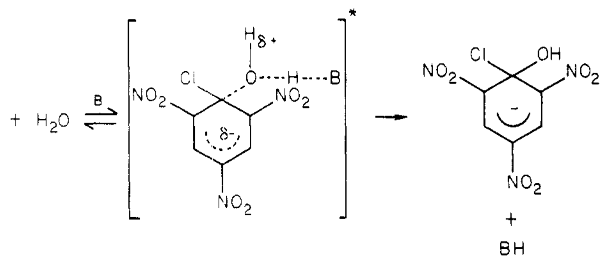


$k_3 >> k_{-2}^{\mathrm{Bi}}; k_2^{\mathrm{Bi}} << k_{-1}$

Scheme III



Scheme IV



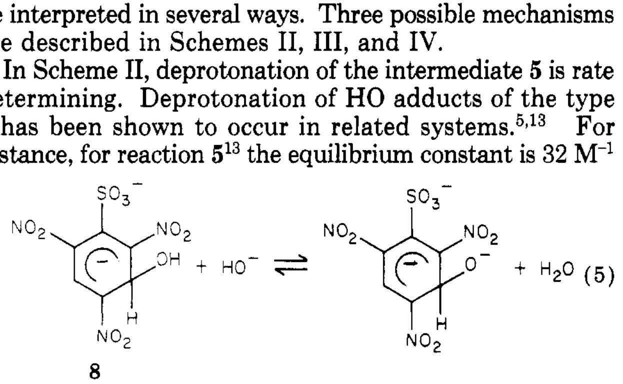
and phosphate represents true base catalysis since these anions may not necessarily behave in the same way as sulfate, it is a good indication of it.

The effect of changing the compensating electrolyte was investigated in the reactions catalyzed by Dabco at one pH. It was found that the slopes of the buffer plots are about the same with $NaNO_3$ or NaCl as electrolyte (Table I).

## Discussion

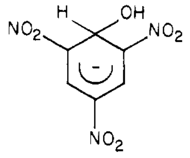
Buffer catalysis in the hydrolysis of picryl chloride can be interpreted in several ways. Three possible mechanisms are described in Schemes II, III, and IV.

In Scheme II, deprotonation of the intermediate **5** is rate determining. Deprotonation of HO adducts of the type **5** has been shown to occur in related systems.[5,13] For instance, for reaction 5[13] the equilibrium constant is 32 $M^{-1}$



**8**

in water at 25 °C, thus the p*K* of **8** is 12.5. This is the highest value to be expected for the p*K* of intermediate **5**, since intermediate **8** bears a negative charge which should increase its p*K* relative to **5**, and in **5** there is an $\alpha$ chlorine which further decreases the p*K*. We can now estimate the order of magnitude of $k_{-1}$ and $k_2^{\mathrm{Bi}}$ in Scheme II. $k_{-1}$ should be similar to the rate of departure of $OH^-$ from compound **9**, i.e., 8 $s^{-1}$.[14] The proton transfer rate, $k_2^{\mathrm{Bi}}$, is given by eq 6. Assuming a $pK_a$ of 12 for **5**, with



**9**

$$k_2^{\mathrm{Bi}} = k_{\mathrm{OH}}[\mathrm{OH}] + k_{\mathrm{Bi}}[\mathrm{Bi}] \qquad (6)$$

Dabco as catalyst ($pK_a = 9.2$), the rate of protonation of **6** by $DabcoH^+$ should be close to that of diffusion,[15] i.e., $10^{10}\ M^{-1}\ s^{-1}$. We can then calculate $k_{\mathrm{Dabco}} \approx 10^{7.2}\ M^{-1}\ s^{-1}$. At pH 9.2 and with $k_{\mathrm{OH}} = 10^{10}\ M^{-1}\ s^{-1}$ we get $k_{\mathrm{OH}}[\mathrm{OH}] \approx 1.6 \times 10^4\ s^{-1}$. Since the concentration of Dabco used was 0.01–0.10 M, $k_2^{\mathrm{Bi}}$ is, under all conditions, higher than $k_{-1}$. The same situation holds for higher and lower pH, which rules out mechanism II. Besides, this mechanism calls for second-order dependence on $OH^-$ concentration, contrary to our experimental finding.

Distinguishing between mechanisms III and IV is more difficult. Mechanism III represents nucleophilic catalysis, whereas mechansim IV is general base catalysis of the water addition step.

If mechanism III is operating, the term $k_B$ in eq 1 can be accounted for by either of the following two situations. (a) $k_1$ is rate determining, and $k_B$ represents the rate of reaction of the base with **2**. (b) $k_1 \gg k_2$, and the process involving the conversion of **7** into picric acid is general base catalyzed; in other words, what one actually measures is the second reaction in Scheme III.[16]

The latter alternative can easily be discarded since in such a case the buffer-independent rate constant should be different for each catalyst because it pertains to the hydrolysis of different substrates. In the reactions reported in this paper the second-order buffer-independent rate constant ($k_{\mathrm{OH}}$, eq 1) is independent of the catalyst within experimental error.

With 2,4,6-trimethylpyridine the kinetic behavior, i.e., the biphasic ln $\Delta$OD vs. time plots, seems to indicate that the mechanism described in Scheme III holds, though in this case the rates of formation and decomposition of the intermediate are similar. It is known that pyridine reacts with picryl chloride to catalyze the rate of hydrolysis,[17] but rate constants are not reported.

For 1-fluoro-2,4-dinitrobenzene the relative rates of reaction with $OH^-$ and pyridine are about 23;[17] if the same relationship holds for picryl chloride, at pH 7.39, $k_{\mathrm{OH}}\cdot[\mathrm{OH}^-]/k_{\mathrm{Pyr}}[\mathrm{Pyr}] \approx 3.10^{-5}$. Even if 2,4,6-trimethylpyridine is $10^5$ times less reactive than pyridine, it can compete with $OH^-$ at the pH of our studies (7.38 and 8). The relative rates of reaction of pyridine and 2,4,6-trimethylpyridine with 2,4-dinitrophenyl *p*-toluenesulfonate are about 10;[18] thus it seems possible that 2,4,6-trimethylpyridine reacts with picryl chloride as a nucleophile, and the intermediate

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(13) M. R. Crampton, *J. Chem. Soc., Perkin Trans. 2*, 343 (1978).

(14) C. F. Bernasconi, *J. Am. Chem. Soc.*, **92**, 4682 (1970).

(15) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).

(16) C. F. Bernasconi, "Relaxation Kinetics", Academic Press, New York, 1976, p 146.

(17) M. M. Joël Lelièvre, R. Gaboriaud, and R. Schaal, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **281**, 155 (1975).

(18) A. Kirkien-Konasiewicz, G. M. Sammy, and A. Maccoll, *J. Chem. Soc. B*, 1364 (1968).

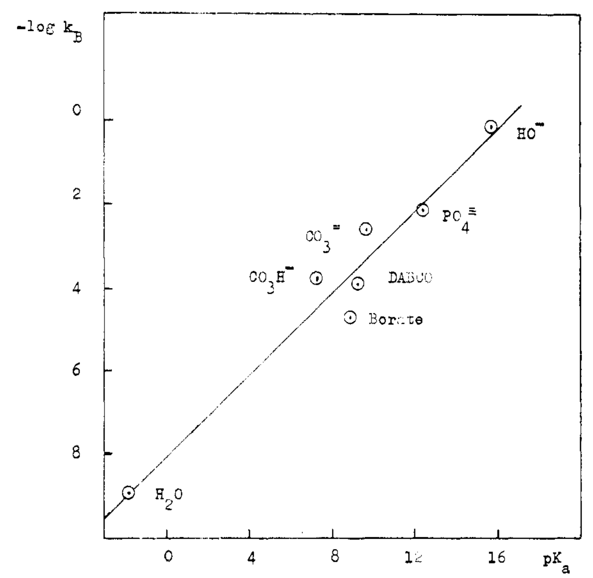

**Figure 3.** Br$\phi$nsted plot for catalysis by general bases; p$K_a$ not statistically corrected, 25 °C, $\mu$ = 1 M.

formed reacts further with $OH^-$ to give picric acid.

The rate of hydrolysis calculated for 4 is 96 times the uncatalyzed rate of hydrolysis of picryl chloride as expected, considering the higher inductive effect at the point of attack by the nucleophile.

*N*-Ethylmorpholine certainly reacts with picryl chloride and can be considered a nucleophilic catalyst.

Dabco is a poorer catalyst than any other of the tertiary amines, and the formation of an intermediate was not detected either kinetically or spectroscopically. If it was reacting through mechanism III, we would expect it to be more reactive than *N*-ethylmorpholine, since it is more basic and less sterically hindered.

We tried to correlate our data on catalysis by bases (Table II) for which nucleophilic catalysis is not obvious, by the Br$\phi$nsted equation (Figure 3). Dabco and phosphate fall on the same line of slope, $\beta$ = 0.5, as water and $OH^-$, whereas carbonate and bicarbonate are about one unit above the line, and borate is two units below. Abnormally high reactivity of carbonate and bicarbonate was previously found in a related system[5] and was interpreted as nucleophilic catalysis. The lower catalytic activity of phosphate and Dabco may be due to the fact that they are acting as general base catalysts (mechanism IV), whereas the others are nucleophilic catalysts (mechanism III).

An additional piece of evidence which indicates that Dabco acts as a general base catalyst and not as a nucleophile is the fact that it has been shown to be very unreactive as a nucleophile toward picryl chloride in benzene,[19] and if it would have reacted, other products would be expected.[20] Moreover, general base catalyzed addition of water to several electrophiles is a well-documented reaction.[5,21]

Although $HO^-$ lies on the same Br$\phi$nsted line defined by Dabco and phosphate, we do not think it acts as a general base catalyst for the reaction of water, since according to the rule formulated by Jencks,[22] general base catalysis is not expected to occur since the reaction of hydroxide ion with water in a simple proton-transfer exchange does not involve an unfavorable free energy change.[23]

The limited number of bases studied and their different structural classes preclude a more detailed discussion.

## Experimental Section

**Materials.** Picryl chloride was recrystallized from ethanol; mp 80–81 °C. Dabco was twice recrystallized from petroleum ether (bp 60–80 °C); mp 155–156 °C. *N*-Ethylmorpholine was treated with phthalic anhydride to remove traces of secondary amines and was distilled under vacuum; bp 46 °C (26 torr). 2,4,6-Trimethylpyridine was distilled under vacuum; bp 65 °C (31 torr). Dioxane was purified by the method of Fieser[24] and was stored over $LiAlH_4$ from which it was distilled as needed. All glass bidistilled water was used throughout.

All the inorganic salts were reagent grade commercial reagents and were used without further purification.

UV spectra were recorded on a Beckmann 24 spectrophotometer, and the change in optical density during a kinetic run was measured on the same instrument at the maximum absorption of picric acid, $\lambda$ = 358 nm.

pH measurements were carried out on a Seybold digital pH meter at 25 °C. Standard buffers prepared according to literature[25] were used to calibrate the electrode.

**Kinetic Procedures.** Rate constants were determined by following the appearance of picric acid [$\lambda_{max}$ = 358 nm ($\epsilon$ 15000)] at 25 °C and $\mu$ = 1 M. All kinetic runs were carried out under pseudo-first-order conditions with substrate concentrations of about $5 \times 10^{-5}$–$4 \times 10^{-4}$ M. Rate constants are accurate to ±3% and were computed from the plots of ln ($OD_\infty - OD_t$) vs. time. Most reactions were followed to 80–90% conversion, but for the slowest runs the reaction was followed up to 10–50% conversion, and the infinity value was calculated from the extinction coefficient of the product.

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**Registry No.** Picryl chloride, 88-88-0; Dabco, 280-57-9; *N*-ethylmorpholine, 100-74-3; 2,4,6-trimethylpyridine, 108-75-8; hydrogen carbonate, 71-52-3; carbonate, 3812-32-6; phosphate, 14265-44-2; hydroxide, 14280-30-9; sodium sulfate, 7757-82-6.

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[19] R. Minetti and A. Bruylants, *Bull. Cl. Sci., Acad. R. Belg*, **56**, 1047 (1970).

[20] S. Ross, J. J. Bruno, and R. C. Petersen, *J. Am. Chem. Soc.*, **85**, 3999 (1963).

[21] W. P. Jencks and H. Gravitz, *J. Am. Chem. Soc.*, **96**, 489 (1974); J. H. Ride, P. A. H. Wyatt, and T. M. Tochowske, *J. Chem. Soc., Perkin Trans. 2*, 1188 (1974).

[22] W. P. Jencks, *J. Am. Chem. Soc.*, **94**, 4731 (1972).

[23] See, however, C. D. Ritchie, D. J. Wright, D. Shing-Huang and A. A. Kamego, *J. Am. Chem. Soc.*, **97**, 1163, 1170 (1975).

[24] L. F. Fieser, "Experiments in Organic Chemistry", 2nd ed., D. R. Heath, Boston, 1941, p 360.

[25] (a) "Analytical Chemistry—The Working Tools", Vol. I, C. R. N. Strauts, J. H. Gilfillan and H. N. Wilson, Ed., Oxford University Press, London, 1958, pp 228–33; (b) R. A. Robinson and R. H. Stokes, "Handbook of Chemistry and Physics", R. C. Weast, Ed., 56th ed., C. R. C. Press, 1975–1976, p D-133.