

249. *The Methanolysis of Nitrophenyl Esters. Part I. The Kinetics of the Transesterification of Picryl Acetate and Benzoate.*

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The kinetics of the methanolysis of picryl acetate and picryl benzoate have been studied under initially neutral conditions and also in the presence of tertiary bases. In the case of the acetate, acyl-oxygen fission occurs uniquely under neutral and basic conditions, and strong base catalysis is observed. For the benzoate, however, there is simultaneous acyl- and alkyl-oxygen fission under neutral conditions, whereas only the former is observed under basic conditions; in this case, too, strong catalysis by tertiary bases is observed. It is concluded that these reactions are further examples of nucleophilic catalysis. Comparisons are made with other systems which undergo base-catalysed methanolysis.

It was shown earlier that γ -phenyltetronic acid enol esters undergo methanolysis, both under initially neutral conditions and in the presence of tertiary bases;^{1,2} there is no evidence for catalysis by acids. γ -Phenyltetronic acid enol benzoate¹ affords an example of general base-catalysis, following the Brønsted law.³ γ -Phenyltetronic acid enol acetate, on the other hand, shows nucleophilic catalysis.² For the tetronic acid enol esters, the alcoholic part is markedly acidic, and so the esters may be compared to acid anhydrides; indeed, methanolysis of the benzoate shows some similarity to the corresponding reaction of acetic anhydride. This will also hold for nitrophenyl esters. Bender and Turnquest⁴ suggested, following Wiberg,⁵ that general base-catalysis is to be expected where the stability (basicity) of the anion from the ester is at least comparable to that of the attacking base. Even in methanol, picric acid is a relatively strong acid,⁶ with $K_a = 1.8 \times 10^{-4}$ at 25°, so that nitrophenyl esters should prove an interesting series in which to study the methanolysis of esters with good leaving groups.

¹ Konasiewicz and Maccoll, *J.*, 1961, 5421.

² Konasiewicz, *J.*, 1961, 5430.

³ Brønsted, *Chem. Rev.*, 1928, 5, 322.

⁴ Bender and Turnquest, *J. Amer. Chem. Soc.*, 1957, 79, 1656.

⁵ Wiberg, *J. Amer. Chem. Soc.*, 1955, 77, 2519.

⁶ Goldschmidt, *Z. phys. Chem.*, 1916, 91, 46.

In previous work on nitrophenyl esters aqueous solvents have been used. Thus, Olivier and Berger⁷ studied the hydrolysis of picryl acetate at 20°, with 50% aqueous acetone as solvent and hydrochloric acid as a catalyst. In view of the very small effect produced by the acid, it can only be concluded that acid catalysis, if present, is extremely weak. The neutral second-order rate constant (k_2^N) is 3.1×10^{-5} l. mole⁻¹ sec.⁻¹. Hinshelwood and Tommila⁸ studied benzyl, phenyl, and *p*-nitrophenyl acetates, under basic and acidic conditions, using 60% acetone-water. The results showed that the acidity of the alcohol part of the ester has little effect on acid hydrolysis but has a very marked effect on alkaline hydrolysis. Bruce and Lapinsky,⁹ for *p*-nitrophenyl acetate at 30°, found $k_2^{\text{OH}^-}$ to be 16.5 and $k_2^{\text{H}_2\text{O}}$ to be 2.6×10^{-8} l. mole⁻¹ sec.⁻¹, in 28.5% ethanol-water. This value for $k_2^{\text{OH}^-}$ is in reasonable agreement with that (12.8 l. mole⁻¹ sec.⁻¹) calculated from the Arrhenius equation.⁸ Bender and Turnquest⁴ showed that the hydrolysis of *p*-nitrophenyl acetate in 5% dioxan-water obeyed the Brønsted relationship for the tertiary base pyridine and its methyl derivatives. However, the rate constants found were vastly greater than those reported by Bruce and Lapinsky.⁹ Bender and Turnquest⁴ showed in addition that the hydrolysis of 2,4-dinitrophenyl acetate was also catalysed by bases, under conditions where esters of weakly acidic alcohols showed no such catalysis. Jencks and Carriuolo,¹⁰ with water as solvent at 25°, found for *p*-nitrophenyl acetate that $k_2^{\text{OH}^-}$ and $k_2^{\text{H}_2\text{O}}$ were 14.8 and 1×10^{-8} l. mole⁻¹ sec.⁻¹, in good agreement with the values of other workers.^{8,9} They also showed that, for a wide range of bases, the hydrolysis of *p*-nitrophenyl acetate obeyed the Brønsted relationship.

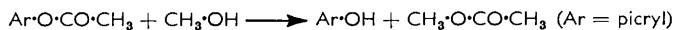
A number of conclusions follow from these results. In the first place, hydrolysis of *p*-nitrophenyl acetate is not particularly sensitive to solvent. Thus, for 60% acetone-water and 28.5% ethanol-water at 30°, the values of $k_2^{\text{OH}^-}$ are 12.8⁸ and 16.5 l. mole⁻¹ sec.^{-1,9} while for 60% acetone-water and water at 25° the corresponding values of 8.1⁸ and 14.8 l. mole⁻¹ sec.^{-1,10} Secondly, nitrophenyl esters show specific hydroxide-ion catalysis, and also general or nucleophilic catalysis by tertiary bases. Thirdly, successive nitro-groups markedly enhance the rate of both neutral and base-catalysed hydrolysis. Thus *p*-nitrophenyl acetate undergoes basic hydrolysis at 25°, about fifteen times faster than phenyl acetate,³ while picryl acetate undergoes neutral hydrolysis at 20°, some three thousand times faster than *p*-nitrophenyl acetate at 25°.

It was decided to study the neutral and base-catalysed methanolysis of a series of nitrophenyl esters, in order to gain further insight into the mechanism of these reactions. Methanol was chosen so that the complexities of kinetics in mixed solvents would be absent. The present Paper describes the study of the methanolysis of picryl acetate and picryl benzoate both under initially neutral conditions and in the presence of tertiary bases.

RESULTS

The Neutral Methanolysis of Picryl Acetate.—Picryl acetate was prepared by dissolving picric acid in acetic anhydride and adding a few drops of perchloric acid. The mixture was poured into water, and the solid, after several recrystallisations from light petroleum (b. p. 60–80°), had m. p. 96° (lit.,^{7,11} 72 and 96°) (C, 35.4; H, 2.1; N, 15.7; O, 46.7. C₆H₃N₃O₈ requires C, 35.5; H, 1.85; N, 15.5; O, 47.2%).

Picryl acetate is nearly colourless,⁷ while picric acid is deep yellow in methanol solution, having an absorption maximum at 3550 Å and a shoulder at 3800 Å. Spectrophotometric analysis of the products showed that acyl-oxygen fission occurred, yielding picric acid and methyl acetate. The picric acid cannot have been produced through the intermediate



⁷ Olivier and Berger, *Rec. Trav. chim.*, 1927, **40**, 609.

⁸ Hinshelwood and Tommila, *J.*, 1938, 1801.

⁹ Bruce and Lapinski, *J. Amer. Chem. Soc.*, 1958, **80**, 2265.

¹⁰ Jencks and Carriuolo, *J. Amer. Chem. Soc.*, 1960, **82**, 1778.

¹¹ Tommasi and David, *Annalen*, 1873, **169–170**, 167; *Compt. rend.*, 1873, **77**, 267; Hantzsch, *Ber.*, 1906, **39**, 1084.

methyl 2,4,6-trinitrophenyl ether (produced by alkyl-oxygen fission) since the rate of methanolysis of this compound to picric acid is negligible compared with that of picryl acetate.¹² As picric acid is a relatively strong acid, the course of the reaction was followed by conductance measurements, as previously described.^{1,2} Good calibration curves were obtained when the specific conductance was plotted against the concentration of picric acid, in the range 0—10 mmoles l.⁻¹. Table 1 shows values of $(C_{\infty})_{\text{obs.}}/(C_{\infty})_{\text{calc.}}$ calculated from the weight of ester taken compared with the values obtained from the specific conductance. These five give an average value of 0.99, confirming the proposed stoichiometry of the reaction.

TABLE 1.

Infinity values for the methanolysis of picryl acetate.

Temp.	0°	25.1°	34.8°	44.6°	54.1°
No. of runs	3	5	3	4	5
$(C_{\infty})_{\text{obs.}}/(C_{\infty})_{\text{calc.}}$	0.96	1.01	1.01	0.97	1.01

The first-order character of the reaction (Table 2) follows from the fact that the percentage of reaction at a given time does not depend on initial concentration, and the first-order rate coefficients are constant over a concentration range of 1.4—10 mmoles l.⁻¹. Good first-order

TABLE 2.

Percentage of reaction with time, at 54.1°.

C_{∞} (mmoles l. ⁻¹)	Time (min.)						$10^6 k_1$ (sec. ⁻¹)
	1	2	3	4	5	6	
1.44	28.5	—	57.0	71.0	80.0	89.0	5320
1.97	30.4	47.1	61.5	68.6	76.5	81.8	5270
4.50	27.2	47.1	60.2	71.0	78.7	85.0	5420
6.35	26.3	44.9	58.7	69.3	77.5	82.7	5010
10.00	31.2	49.9	62.4	73.1	82.5	90.0	5300
Mean	28.7	47.2	59.8	70.6	79.0	85.7	5260

plots were obtained. To verify that the rate of methanolysis was unaffected by the platinum electrodes, two runs were done in a cell of constant 0.67 cm.⁻¹, as compared with the normal cells of constants 0.05—0.08 cm.⁻¹. The rate constants at 0° were 7.75 and 7.76×10^{-6} sec.⁻¹ as compared with the mean value 7.29×10^{-6} sec.⁻¹ obtained with the normal cells. The variation of the rate constant with temperature (Table 3) led to the Arrhenius equation, $\log k_1 = 12.239 - 21,750/2.303 RT$, which fitted the experimental points excellently. If the

TABLE 3.

The variation of k_1 with temperature.

Temp.	0°	25.1°	34.8°	44.6°	54.1°
No. of runs	6	5	3	4	5
$10^6 k_1$ (sec. ⁻¹)	7.29	209	687	2030	5260

reaction were due to specific methoxide-ion catalysis, the first-order rate coefficients would be expected to fall as the reaction proceeded, and picric acid was produced. This was not observed. Also, a run done in the presence of 5 mmoles l.⁻¹ of picric acid at 0° had $10^6 k_1 = 7.0$ sec.⁻¹, to be compared with the mean value of 7.29 sec.⁻¹ for runs in the absence of initially added picric acid. Specific methoxide-ion catalysis thus does not occur.

The Base-catalysed Methanolysis of Picryl Acetate.—To see whether the reaction was base-catalysed, runs were carried out in the presence of pyridine and its 2-methyl, 2,6-dimethyl, and 2,4,6-trimethyl derivatives (2-picoline, 2,6-lutidine, and 2,4,6-collidine). First-order rate coefficients showed a marked decrease during the course of a run, but, provided that the concentration of the base was greater than or equal to the picryl acetate concentration, constant second-order rate coefficients were obtained from the formula $k_2 t = (a - b)^{-1} \ln a(b - x)/b(a - x)$. Where the base concentration was less than the initial concentration of ester, initial second-order rate coefficients were calculated. The results are shown in Table 4. There is no significant trend of rate constant with either ester or base concentration in the

¹² Konasiewicz and Maccoll, unpublished results.

TABLE 4.

Catalysis by pyridine at 0°.

Ester (mmoles l. ⁻¹)	1.28	2.17	2.30	4.60	2.80	2.86	4.95
Base (mmoles l. ⁻¹)	0.625	0.625	2.00	2.00	5.00	5.00	5.00
10 ⁴ k ₂ ^B (l. mole ⁻¹ sec. ⁻¹)	7.1	8.0	7.1	8.9	7.8	7.1	8.7

concentration ranges 1.3—4.95 and 0.6—5.00 mmoles l.⁻¹, respectively, the average value of k₂^B being 7.81 × 10⁻¹ l. mole⁻¹ sec.⁻¹. In the presence of the bases 2-picoline, 2,6-lutidine, and 2,4,6-collidine, the rate coefficients (Table 5) were again independent of the initial concentrations of both base and ester.

TABLE 5.

The effects of methyl-substituted pyridines at 0°.

Base	Pyridine	2-Picoline	2,6-Lutidine	2,4,6-Collidine	Methanol
No. of runs	7	4	4	4	6
10 ⁴ k ₂ ^B (l. mole ⁻¹ sec. ⁻¹)	78.1	3.80	1.01	27.9	2.9 × 10 ⁻⁵

The Neutral Methanolysis of Picryl Benzoate.—Picryl benzoate, prepared by heating benzoyl chloride and picric acid at 180—200° for two hours,¹³ had m. p. 162—163° (from chloroform) (lit.,¹³ 163—164°) (C, 46.8; H, 2.4; N, 12.7. Calc. for C₁₃H₇N₃O₃: C, 47.0; H, 2.1; N, 12.6%). Initially the overall stoichiometry of the reaction appeared to be:



on the basis of picric acid produced; that is, acyl-oxygen fission occurred. This was borne out by the infinity values (Table 6) which were estimated by both conductance and optical density measurements. The agreement is reasonable, considering that the values were taken after the cells had been in the thermostat for some 700 hours. Examination of the concentration-

TABLE 6.

Values of C_∞ mmoles l.⁻¹ at 54.1°.

Calculated	8.29	4.70	2.44	1.95
Observed (optical density)	8.45	4.95	—	1.86
Observed (conductance)	8.45	5.30	2.54	1.85

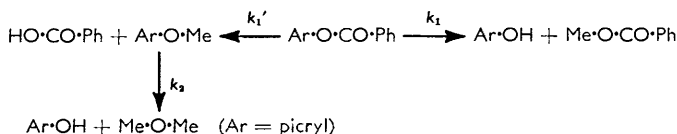
time curves (Fig. 1) and a first-order plot (Fig. 2) showed that the reaction was not simple. The first-order rate coefficient decreased markedly as the reaction proceeded. However, the fraction decomposed at a given time was independent of the initial concentration (Table 7), and this suggested a combination of first-order processes.

TABLE 7.

The course of methanolysis of phenyl benzoate.

Initial concn. (mmoles l. ⁻¹)	Time (hr.)			
	5	10	15	20
1.94	0.232	0.331	0.371	0.445
2.44	0.197	0.304	0.384	0.431
4.70	0.202	0.321	0.395	0.449
8.29	0.185	0.314	0.385	0.452
Mean	0.204	0.318	0.384	0.444

An obvious explanation of the experimental results is the occurrence of alkyl-oxygen along with acyl-oxygen fission, the latter yielding methyl 2,4,6-trinitrophenyl ether which reacts further to form picric acid. Simultaneous alkyl- and acyl-oxygen fission has been observed, for example, in the alkaline hydrolysis of the methyl ester of 2,4,6-triphenylbenzoic acid.¹⁴ The reaction scheme would then be:



¹³ Laurent and Gerhardt, *Annalen*, 1850, **75**, 75; Kym, *Ber.*, 1898, **32**, 1427.

¹⁴ Bunton, Comyns, Graham, and Quayle, *J.*, 1955, 3817.

The benzoic acid would then undergo esterification by the methanol in the presence of picric acid during the long time required for the reaction to reach completion. The presence of methyl 2,4,6-trinitrophenyl ether in the reaction mixture was confirmed by the red colour (Meisenheimer complex) produced by sodium hydroxide. Picryl benzoate on similar treatment gave a yellow colour. An estimate of the rate of methanolysis of methyl 2,4,6-trinitrophenyl ether was made by studying the reaction in the presence of pyridine and plotting initial first-order rate constants against base concentration and extrapolating to zero base. The rate of the neutral methanolysis obtained in this way was 2.0×10^{-6} sec.⁻¹, compared with the mean value of 1.9×10^{-6} sec.⁻¹ inferred from the study of the neutral methanolysis of picryl benzoate. The agreement between these two values confirms the proposed mechanism.

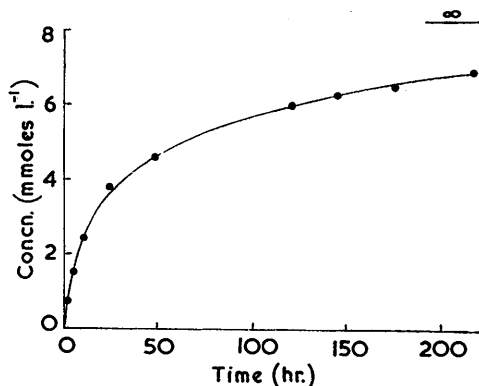


FIG. 1. The rate of production of picric acid from picryl benzoate in methanol at 54.1°.

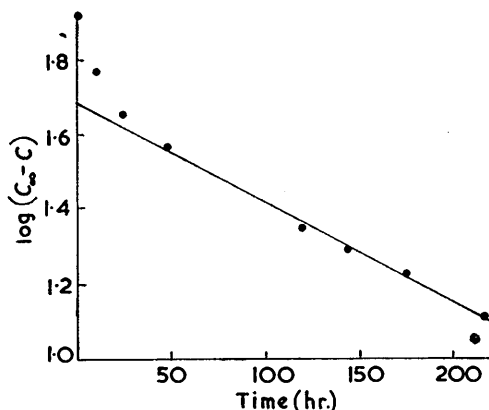


FIG. 2. A plot of the logarithm of the picric acid concentration against time for the run shown in Fig. 1.

If the concentration of picric acid is $[P]$, and the initial concentration of picryl benzoate is b , then,

$$\frac{[P]}{b} = 1 - \frac{k_1 - k_2}{k_1 + k_1' - k_2} \exp\{- (k_1 + k_1')t\} - \frac{k_1'}{k_1 + k_1' - k_2} \exp\{-k_2 t\} \quad (1)$$

If $k_2 < k_1$ and k_1' , this reduces to

$$[P]/b = \{(k_1 - k_2)/(k_1 + k_1' - k_2)\} \{1 - \exp[-(k_1 + k_1')t]\} \quad (2)$$

From eqn. (2) we get

$$\log \{(k_1 - k_2)/(k_1 + k_1' - k_2) - [P]b\} = - (k_1 + k_1')t \quad (3)$$

and so a plot of the logarithmic term against t gives a straight line of slope $-(k_1 + k_1')/2.303$. Approximation to k_1 and k_1' may be obtained from the relationships

$$k_1 = b^{-1}(d[P]/dt)_0 \text{ and } k_1/(k_1 + k_1') = -b^{-1}(d^2[P]/dt^2)_0 \quad (4)$$

obtained by neglecting k_2 in comparison with k_1 and k_1' , or, better, from the initial slopes of a plot of $\log(b - [P])$ against t and its first differential, using

$$2.303\{d \log(b - [P])/dt\}_0 = k_1, \text{ and } 2.303\{d^2 \log(b - [P])/dt^2\}_0 = k_1 k_1' \quad (5)$$

Further, if t is large and $k_2 < k_1 + k_1'$, eqn. (1) reduces to

$$[P]/b = 1 - \{k_1'/(k_1 + k_1' - k_2)\} \exp\{-k_2 t\} \quad (6)$$

and so a plot of $\log(b - [P])$ against t should give a straight line of slope $-k_2/2.303$ and an intercept at $t = 0$ of $\log\{bk_1'/(k_1 + k_1' - k_2)\}$.

The set of experimental points (Table 8) leads to the trial values $10^5 k_1 = 1.38$, and $10^5 k_1' =$

TABLE 8.

The rate of production of picric acid.

Time (hr.)	0	1	2	3	4	5	6	7	8	9	10
$P_{\text{obs.}}$ (mmoles l. ⁻¹)	0.05	0.44	0.76	1.04	1.29	1.52	1.73	1.93	2.10	2.27	2.43
$P_{\text{calc.}}$ (mmoles l. ⁻¹)	0	0.39	0.77	1.03	1.31	1.58	1.75	1.94	2.12	2.25	2.38

2.0 sec.⁻¹. For the same run, eqn. (6) yielded $10^6 k_2 = 1.64 \text{ sec.}^{-1}$, thus justifying the inequality $k_2 < k_1 + k_1'$ and the use of eqn. (3). On substitution into eqn. (3), with $b = 8.29$, the value of $10^5(k_1 + k_1')$ of 3.40 sec.^{-1} was obtained, which, in conjunction with $(k_1 + k_2)/(k_1 + k_1' - k_2) = 0.409$, yielded $10^5 k_1 = 1.48$, and $10^5 k_1' = 1.92 \text{ sec.}^{-1}$. A good linear plot was obtained, indicating a fortunate choice of initial values. In general, if the line is concave upwards, a new, smaller value of $(k_1 - k_2)/(k_1 + k_1' - k_2)$ is chosen and the process repeated. If, on the other hand, the curve is convex upwards, a larger value of the ratio is used. The value of $k_1'(k_1 + k_1' - k_2)$ obtained from eqn. (6) was equal to 0.600, to be compared with the value of 0.591 obtained by the use of eqn. (3). Calculated values of picric acid concentration as a

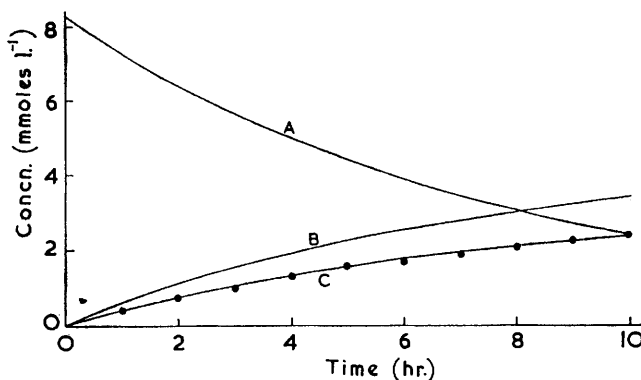


FIG. 3. The concentrations of (A) picryl benzoate, (B) methyl 2,4,6-trinitrophenyl ether, and (C) picric acid, as a function of time, in the methanolysis of picryl benzoate.

function of time are shown in Table 8. In Fig. 3 the variation in the concentrations of picryl benzoate, methyl 2,4,6-trinitrophenyl ether and picric acid with time are shown. Rate constants for all the runs, calculated as described above, are shown in Table 9. The mean values of k_1 , k_1' , and k_2 are 1.63×10^{-5} , 2.00×10^{-5} , and $1.87 \times 10^{-6} \text{ sec.}^{-1}$. It is not considered that there is any systematic trend with initial concentration, outside the limits of experimental error. Three runs were also done in the presence of initially added picric acid. These gave

TABLE 9.

The rate constants of methanolysis at 54.1°.

$[B]$ (mmoles l. ⁻¹)	2.44	4.70	8.29	2.46	2.46	2.46
$[P]$ (mmoles l. ⁻¹)	—	—	—	5.00	2.50	1.25
$10^5 k_1$ (sec. ⁻¹)	1.76	1.65	1.48	1.56	1.36	1.32
$10^5 k_1'$ (sec. ⁻¹)	2.16	1.92	1.92	2.01	1.84	1.89
$10^6 k_2$ (sec. ⁻¹)	2.13	1.84	1.64	—	—	—
$k_1/(k_1 + k_1')$	0.418	0.434	0.409	—	—	—
$k_1'/(k_1 + k_1')$	0.642	0.600	0.600	—	—	—

$10^6 k_1 = 1.41 \text{ sec.}^{-1}$ and $10^6 k_1' = 1.91 \text{ sec.}^{-1}$, which again are not significantly different from the mean values in the absence of picric acid. Two runs were done in 50% v/v acetone-water at 54.1°. Good first-order plots were obtained, giving a mean first-order rate constant of $5.2 \times 10^{-5} \text{ sec.}^{-1}$. When account is taken of the molarity of water, the corresponding second-order rate constant is $1.8 \times 10^{-6} \text{ l. mole}^{-1} \text{ sec.}^{-1}$.

The Base-catalysed Methanolysis of Picryl Benzoate.—As in the case of the acetate, runs were

done in the presence of different concentrations of base. Typical results are shown in Table 10, leading to a mean value of 10^3k_2 of $1.72 \text{ l. mole}^{-1} \text{ sec.}^{-1}$. Varying the base led to the results

TABLE 10.
Catalysis by 2-picoline at 54.1° .

[Ester] (mmoles l.^{-1})	3.08	3.96	5.14	2.04	4.02	8.17
[Base] (mmoles l.^{-1})	10	10	10	20	20	20
10^3k_2 ($\text{l. mole}^{-1} \text{ sec.}^{-1}$)	1.77	1.93	1.92	1.42	1.47	1.85

TABLE 11.
The effects of methyl-substituted pyridines at 54.1° .

Base	Pyridine	2-Picoline	2,6-Lutidine	2,4,6-Collidine	Methanol (acyl-O fission)
Runs	3	6	3	4	6
$10^3k_2^B$	381	17.2	5.95	129	6.1×10^{-4}

shown in Table 11. In no case is there a significant variation of k_2 with concentration of either the base or the ester.

DISCUSSION

The case of picryl acetate is relatively straightforward since the reaction is first-order with respect to acetate and yields picric acid, confirming acyl-oxygen fission. As there is no inhibition of the reaction in the presence of picric acid, specific methoxide-ion catalysis may be eliminated as a possible mechanism. Again, since the catalytic constants k_2^B are not proportional to K_B and do not obey the Brönsted relationship, the strength of the bases being 2,4,6-collidine > 2,6-lutidine > 2-picoline > pyridine, both specific methoxide-ion and general-base catalysis may be eliminated. The reaction is thus probably a further example of nucleophilic catalysis.² It is of interest to compare the rate of methanolysis of picryl acetate with its rate of hydrolysis in 50% aqueous acetone. Oliver and Berger⁷ give, at 20° , the value $5.3 \times 10^{-4} \text{ sec.}^{-1}$, while for methanolysis the value (from the Arrhenius equation reported here) is $1.1 \times 10^{-4} \text{ sec.}^{-1}$. This would suggest that the polarity of the transition state did not markedly differ from that of the initial state.

A number of points emerge when a comparison is made between the behaviour of the acetate and benzoate under both neutral and basic conditions. In the first place, the rate ratio acetate:benzoate is 320:1 (for acyl-oxygen fission at 54°). This greatly exceeds the value found for the $B_{Ac}2$ mechanism, namely 10:1, and that observed for γ -phenyltetronic acid enol acetate and benzoate, namely 6.5:1. Under basic conditions, the relative rates are shown in Table 12. The patterns of behaviour are the same for picryl benzoate and acetate, though both differ from γ -phenyltetronic acid enol acetate in the reversal of the rates for 2-picoline and 2,6-lutidine. A further important difference lies in the enhanced range of catalytic constants in going from 2,6-lutidine to pyridine in the case of the picryl compounds.

TABLE 12.
The relative rates of base-catalysed methanolysis.

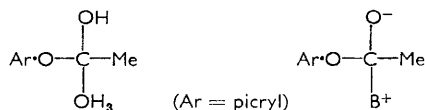
	Pyridine	2,4,6-Collidine	2-Picoline	2,6-Lutidine	Methanol
Picryl acetate (0°)	6.2×10^5	2.1×10^5	2.8×10^4	9.7×10^3	1
Picryl benzoate (54.1°)	2.7×10^6	9.6×10^5	1.3×10^5	3.5×10^4	1
γ -Phenyltetronic (55°) acid enol acetate	7.4×10^3	6.5×10^3	1.1×10^3	3.8×10^3	1
Acetic anhydride ¹⁵ (20°)	1.5×10^3	—	—	—	1

For the acetate, the reaction may be regarded as proceeding through the following intermediates in the case of the neutral and base-catalysed reactions, as in the case of

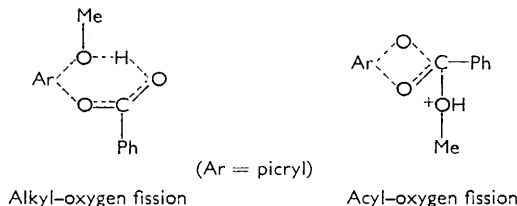
¹⁵ Koskikallio, *Suomen Kem.*, 1959, **32**, B, 41.

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γ -phenyltetronic acid enol acetate, and so the reaction in the presence of bases is essentially nucleophilic catalysis.



The rates of reaction in the presence of methyl-substituted pyridines can be understood in terms of steric hindrance. In the case of the benzoate, however, the very great decrease of rate in substituting phenyl for methyl, and also the simultaneous acyl- and alkyl-oxygen fission, suggest that steric factors have now become so large that a new type of transition state is involved. The following are suggested:



Base-catalysis of the alkyl-oxygen fission was negligible compared with that for acyl-oxygen fission, since in this case the system followed a simple second-order rate law. The reaction in the presence of bases is again regarded as nucleophilic catalysis. The type of transition state postulated for alkyl-oxygen fission resembles the complex formed between methoxide ions and methyl 2,4,6-trinitrophenyl ether.¹⁶ Similar behaviour to that described here for picryl benzoate has been observed by Bevan and Hirst¹⁷ in the case of the methanolysis of picryl chloride. They observed rate coefficients which fell as the reaction proceeded, and also the production of chloride ions as an intermediate, the final product being picric acid. This was explained on the basis that picryl chloride could yield either picric acid and methyl chloride, or methyl 2,4,6-trinitrophenyl ether and hydrogen chloride, which is similar to the scheme suggested here for the methanolysis of picryl benzoate.

We thank Professor C. A. Bunton for helpful discussion, and Professor L. J. Haynes for suggesting the problem and for the loan of apparatus.

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[Received, May 27th, 1963.]

¹⁶ Jackson and Gazzolo, *Amer. Chem. J.*, 1900, **23**, 376; Jackson and Earle, *ibid.*, 1903, **29**, 59; Meisenheimer, *Annalen*, 1902, **323**, 205.

¹⁷ Bevan and Hirst, *J.*, 1956, 254.