

162. *The Salt-forming Characteristics of Doubly- and Singly-linked Elements of the Oxygen Group. Part III. The Carbonyl Group in Ethyl Benzoate.*

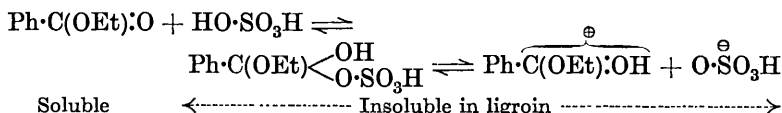
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It has previously been shown (Baker, J., 1931, 307; Baker and Moffitt, *ibid.*, p. 314) that in concentrated sulphuric acid solution, the carbonyl group in benzaldehyde ($R = H$) and acetophenone ($R =$

Me) exists largely in the form of the oxonium salt $\overbrace{-\text{CR}:\text{OH}}^{\oplus} \} \text{HSO}_4^{\ominus}$. The analogous case of ethyl benzoate (R = OEt) has now been studied.

Since this ester gives no colour with concentrated sulphuric acid, a colorimetric method of investigation was excluded,* but application of the partition and nitration methods used before has shown that oxonium salt formation occurs.

By analogy with the systems previously studied, the condition of ethyl benzoate in sulphuric acid solution is most probably represented by the consecutive ionic equilibria :



although it is recognised that, in this case, the possibility of oxonium salt formation involving the singly-linked oxygen of the ethoxy-group, $-\text{C}:\text{O}^{\oplus}\text{HEt}\} \text{X}^{\ominus}$, cannot be excluded. In either case the proportion of the ester present in the unmodified form should be readily determined by partition between ligroin (in which it is miscible in all proportions) and sulphuric acid. The results obtained in such partition experiments at the ordinary temperature are in Table I, the proportion of ester in the ligroin layer being determined by quantitative hydrolysis.

TABLE I.

Partition of ethyl benzoate between sulphuric acid and ligroin at the ordinary temperature.

$\frac{100[\text{H}_2\text{SO}_4]}{[\text{H}_2\text{SO}_4] + [\text{H}_2\text{O}]}$ (Approx.) 3% free SO ₃	$\frac{100[\text{SO}_3]}{[\text{SO}_3] + [\text{H}_2\text{O}]}$ Approx. 82.1	Proportion of Ph·CO ₂ Et in ligroin layer (%)	
		(A) Without (NH ₄) ₂ SO ₄ .	(B) With (NH ₄) ₂ SO ₄ .
100	81.9	2.8	6.4
1—2% " "	81.6	3.2	9.5
90	73.5	5.4	15.5
		11.7	98.1

The close similarity of these results with those obtained in the case of benzaldehyde (Baker, *loc. cit.*) is immediately apparent, addition of ammonium sulphate to the acid layer causing a similar repression of the ionic dissociation, followed by a further decomposition of the pseudo-salt into the free ester and sulphuric acid, with the result that, under these conditions, a much larger proportion of

* Alteration in the nature and position of the ultra-violet absorption bands is under investigation.

the ester is found in the ligroin layer. Comparison of the data for the aldehyde and the ester suggests, however, that this effect is more pronounced in the case of the oxonium salt of ethyl benzoate, which also appears to be more susceptible to hydrolysis as the concentration of the sulphuric acid is diminished.

Even more conclusive evidence of the presence of the oxonium-salt form is found in the large increase in the proportion of *m*-substitution [due to the integral positive charge distributed on the carbonium-oxonium kation, $\text{Ph}\cdot\overset{\oplus}{\text{C}}(\text{OEt})\text{:OH}$], which occurs when ethyl benzoate is nitrated in the presence of sulphuric acid containing free sulphur trioxide (compare Holleman, *Ber.*, 1906, **39**, 1715). The results obtained (details of which are given in the experimental portion) are summarised in Table II.

TABLE II.

Nitration of ethyl benzoate under various conditions.

Nitration No.	Conc. of H ₂ SO ₄ .	Density (<i>d</i> ^{15°}) of HNO ₃ .	Mean proportion of <i>m</i> -isomeride formed (%) (error, ±0.5—1%).	
			(a) Without Am ₂ SO ₄ .	(b) With Am ₂ SO ₄ .
1—2	5.5% free SO ₃	1.53	93.7	85.0
3—4	3.3% „	1.53	92.7	84.7
5—6	100.4% „	1.53	91.4	82.5
7—10	90% „	1.53	82.9	78.8
11	0% „	1.53	74.8	—
12	0% „	1.53 + N ₂ O ₅	75.8	—

The proportion of *m*-nitration observed in nitric acid (*d* 1.53) alone (74.8%: Holleman, "Die direkte Einführung von Substituenten in den Benzolkern," p. 126, records 68.4%) is increased to 93.7% when nitration is effected in the presence of sulphuric acid containing 5.5% of free sulphur trioxide, that is, under conditions which would preclude hydrolysis of the oxonium salt. This value decreases gradually as the concentration of sulphur trioxide is diminished, but, even in 90% sulphuric acid, is still considerably greater than that obtained in absolute nitric acid alone. Moreover, the effect of added ammonium sulphate in repressing the ionisation and so displacing the equilibria in favour of free ethyl benzoate, with a consequent diminution (8—9%) in the proportion of the *m*-nitro-isomeride formed, is even more marked than it is in the cases of benzaldehyde and acetophenone (4—5%), a result fully in agreement with the larger common-ion effect of this reagent noted above in connexion with the partition experiments. Thus it would appear not only that the carbethoxy-group is converted into the oxonium condition in sulphuric acid, but also that nitration in this medium occurs largely through the carbonium-oxonium kation so formed.

In the nitration of ethyl benzoate in absolute nitric acid in the presence of nitric anhydride, it has been suggested (Bassett, *Chem. and Ind.*, 1931, 137) that the removal, by the anhydride present, of water formed during the reaction should prevent any hydrolysis of the hypothetical oxonium nitrate, with the result that a similar increase in the proportion of *m*-isomeride should be observed. It was also suggested that this result was all the more likely since nitric acid is a stronger acid than sulphuric. The last statement, however, is presumably based on the values of the dissociation constants of the two acids ($\alpha = 0.92$ and $\alpha = 0.58$ respectively) *in aqueous solution*. Hantzsch (*Ber.*, 1931, 64, 667), however, has suggested that the strength of an acid is determined by its tendency towards salt formation, and, on this view, the strongest acids have their most marked action as such, and are weakest as their ions in dilute aqueous solution, since there they are present exclusively as hydroxonium salts. Hence sulphuric acid, although, for this reason, a weaker acid than nitric in dilute aqueous solution, is the stronger acid under the nitration conditions employed in this investigation. Thus, as was previously suggested (Baker and Moffitt, *loc. cit.*), the reaction of the carbonyl group with absolute nitric acid probably involves merely the formation of a loose salt-like complex, the consequent augmentation of the positive field around the carbonyl group causing a relatively small increase (Expts. No. 12 and 11) in the proportion of *m*-nitro-compound formed, whereas in sulphuric acid actual formation of an oxonium salt occurs, the *integral* positive charge on the kation of which accounts for the much larger increase (19%; compare Expts. No. 1 and 11) in *m*-nitration observed under these conditions.

EXPERIMENTAL.

Partition Experiments.—These were carried out in a manner similar to that previously described in the case of benzaldehyde, except that the quantity of ester in the ligroin layer was determined by pipetting 10 c.c. of this layer into 25 c.c. of 0.5105*N*-alcoholic potassium hydroxide, hydrolysing the ester on a steam-bath for $\frac{1}{2}$ hour, and titrating the excess of alkali with 0.5*N*-sulphuric acid and phenolphthalein. Preliminary experiments showed that the hydrolysis was quantitative under these conditions.

The results are summarised in Table III.

Nitration of Ethyl Benzoate in the Presence of Sulphuric Acid.—The ester was added slowly with mechanical stirring to the nitration mixture, the temperature being maintained at $5^{\circ} \pm 1^{\circ}$ for about 2 hours. After it had attained the ordinary temperature, the solution was kept for a further 12 hours and then poured on ice and

TABLE III.

Partition of ethyl benzoate between sulphuric acid and ligroin at the ordinary temperature.

Ligroin = 20 c.c. Sulphuric acid = 5 c.c. $(\text{NH}_4)_2\text{SO}_4 = 2 \text{ g.}$

Data relating to ligroin layer.

$\frac{100[\text{H}_2\text{SO}_4]}{[\text{H}_2\text{SO}_4] + [\text{H}_2\text{O}]}$	Ph-CO ₂ Et taken (g.).	0.5105N-KOH for ester in 10 c.c. (c.c.).		Ph-CO ₂ Et in 20 c.c. (g.).		Ph-CO ₂ Et, %.	
		(a)	(b)	(a)	(b)	(a)	(b)
		Without Am ₂ SO ₄ .	With Am ₂ SO ₄ .	(a)	(b)	(a)	(b)
Approx. 3% free SO ₃	1.2128	0.22	0.51	0.0337	0.0781	2.8	6.4
" 1—2% "	1.1606	0.24	0.72	0.0368	0.1103	3.2	9.5
" 100.4%	1.2741	0.45	1.21	0.0689	0.1853	5.4	15.5
" 90%	1.2584	0.96	8.06	0.1470	1.2344	11.7	98.1

an excess of potassium hydrogen carbonate, and the neutral products were extracted with ether. The residue from the dried ethereal extract was desiccated in a vacuum to constant weight. The yield of mononitro-derivatives was over 95% in many cases, but as low as 70—75% in others; in the latter, however, almost the whole of the remaining material was accounted for by acid products. Since no trace of nitrous fumes was observed during the nitrations, these acid products are probably formed by hydrolysis of the ester rather than by oxidation. The tendency towards such hydrolysis seems to increase with increasing strength of sulphuric acid, suggesting that the initial stage is the addition of the sulphuric acid to the ester, a mechanism similar to that suggested by Hantzsch (*loc. cit.*) for the hydrolysis of nitriles to acid amides through the initial formation of nitrilium salts. The agreement in the values for the *m*-content of the neutral mononitration product in Expts. No. 7 and 8, 9 and 10, however, shows that no preferential hydrolysis of any one isomeride occurs, and therefore the formation of acid products in no way impairs the validity of the results obtained in such cases. The numerical details, except analyses, of nitrations in the presence of sulphuric acid are recorded in Table IV.

Nitration of Ethyl Benzoate in Nitric Acid.—In Expt. No. 11 the ester was added slowly with mechanical stirring to nitric acid (*d* 1.53) at -10° to -5° during 0.5 hour. The reaction mixture was kept at this temperature for a further 0.7 hour and then poured on ice and potassium hydrogen carbonate and worked up as recorded above. In Expt. No. 12 the essential conditions were the same, except that the nitration medium consisted of absolute nitric acid (*d* 1.53) together with a large excess of freshly distilled nitrogen pentoxide prepared in the usual manner. The results are in Table IV.

TABLE IV.

Nitration No.	Ph·CO ₂ Et taken (g.).	HNO ₃ (<i>d</i> ¹⁵ 1.53) (g.).	H ₂ SO ₄ (g.).	Conc. of H ₂ SO ₄ free SO ₃	Am ₂ SO ₄ added (g.).	Product (g.).	
						Neut.	Acid.
1	4.231	3	70	5.5%	0	3.705	1.414
2	4.222	3	70	5.5%	12	3.939	1.256
3	4.340	3	60	3.3%	0	4.788	—
4	4.657	3	60	3.3%	12	5.750	—
5	2.980	2.2	45	100.4%	0	2.915	0.796
6	2.967	2.2	45	100.4%	9	3.445	0.302
7	4.133	3	80	90%	0	4.265	0.537
8	3.169	3	60	90%	0	3.973	—
9	4.144	3	80	90%	12	4.238	0.433
10	3.080	3	60	90%	12	3.786	—
*11	3.304	25	0	—	—	4.132	—
†12	2.920	+N ₂ O ₅ =25	0	—	—	3.803	—

* -10° to -5° for 1.2 hrs.

† -10° to -15° for 1.75 hrs.

TABLE V.

Nitration No.	Neutral product hydrolysed (g.).	Recovered (g.).					Composition of acids.					
		Acids		C ₆ H ₄ ·CO ₂ H.	C ₆ H ₃ Br·NH ₂ .	C ₆ H ₃ Br ₂ ·CO ₂ H.	R·CO ₂ H (mols. %).			Nitro-isomerides, %.		
		ob-tained (g.).	separated (g.).				R =					
							C ₆ H ₄ .	NO ₂ ·C ₆ H ₄ .	m.	op.	m.	
1	2.241	1.868	0.568	0.014	0.062	1.051	3.7	6.0	90.3	6.3	93.7	
2	2.188	1.791	0.569	0.013	0.152	0.969	3.4	14.6	82.0	15.0	85.0	
3	2.513	2.130	0.592	0.006	0.074	1.139	1.5	6.7	91.8	6.8	93.2	
4	2.790	2.363	0.796	0.009	0.113	1.513	1.6	7.7	90.7	7.8	92.2	
			0.640	0.008	0.189	1.162	1.7	15.3	83.0	15.5	84.5	
5	2.339	1.983	0.711	0.009	0.201	1.286	1.8	14.8	83.4	15.0	85.0	
6	2.266	1.941	0.635	0.014	0.102	1.229	3.1	8.3	88.6	8.6	91.4	
7	2.434	2.046	0.563	0.005	0.175	0.969	1.3	16.8	81.9	16.9	83.1	
8	2.584	2.190	0.704	0.008	0.223	1.253	1.6	17.1	81.3	17.4	82.6	
9	2.548	2.154	0.608	0.008	0.236	1.011	1.9	20.5	77.6	20.9	79.1	
10	2.887	2.773	0.703(5)	0.005	0.287	1.185	1.0	21.3	77.7	21.6	78.4	
11	2.811	2.658	0.943	0.008	0.455	1.529	1.2	24.9	73.9	25.2	74.8	
12	2.366	2.286	0.829	0.013	0.343	1.210	2.4	23.7	74.9	24.2	75.8	

Determination of the Proportion of Isomerides formed.—A weighed portion (2—3 g.) of the neutral mononitration product was hydrolysed by boiling with 50 c.c. of 10% aqueous potassium hydroxide for 0.5 hour and the resulting mixed nitrobenzoic acids were analysed by the bromination method of Flürscheim and Holmes (J., 1928, 448) in the usual manner. The results are in Table V.

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