XLII.—*The Salt-forming Characteristics of Doubly- and Singly-linked Elements of the Oxygen Group. Part II. Nitration of Benzaldehyde and Acetophenone in Sulphuric Acid Solution.*

By JOHN WILLIAM BAKER and WILLIAM GEORGE MOFFITT.

IT has been clearly established (Baker and Ingold, J., 1930, 431; compare Baker, J., 1928, 1281) that the conversion of an azomethine system, $-\text{CR}{:}\text{NR}'$, attached to an aromatic nucleus into its salt causes strong *m*-orientation resulting from the partial transference of the kationic charge to the α-carbon atom of the side chain. Moreover, on nitration of benzylidene-anils in sulphuric acid solution, the proportion of the *m*-isomeride formed is depressed by the addition of ammonium sulphate to the nitrating medium. This depression was ascribed to the well-known common-ion effect, the change ion ⟶ salt being succeeded in the case of such ψ-basic systems by the further *m*-repressing influence due to the partial conversion of this salt into the ψ-salt or the neutral form (*loc. cit.*, p. 434). Thus the conclusions concerning the existence of benzaldehyde and acetophenone as oxonium salts in sulphuric acid solution which have been reached on the basis of physical measurements (preceding paper) should be capable of verification by an investigation of the proportion of the *m*-isomeride formed when these substances are nitrated in the presence of a large excess of concentrated or fuming sulphuric acid, *i.e.*, under conditions conducive to the stability of the oxonium salt. The results of such an investigation are now described.

In its neutral condition, the *m*-directive influence of the carbonyl group has been ascribed to the presence of the fractional dipole $-\overset{\delta+}{\text{C}}=\overset{\delta-}{\text{O}}$ (Baker and Ingold, J., 1927, 832). In acid media, however, a tendency for the oxygen to co-ordinate a proton and form a salt-like complex may be anticipated. This would increase the positive charge on the group and thus enhance its *m*-directive power. Such reaction with the acid medium may involve merely the formation of a loose salt-like complex, with the consequent augmentation of the positive field around the carbonyl group by a mechanism similar to that postulated for the attack of an acid catalyst in the mutarotation of sugar derivatives (Baker, J., 1928, 1586), or it may result, in the presence of large concentrations of sulphuric acid, for example, in the actual formation of the oxonium salt $\left.Ph{\cdot}\overbrace{CR{:}OH}^{\oplus}\right\}\overset{\ominus}{X}$, in which case the *integral* positive charge on the kation will cause a very high proportion of *m*-substitution. The increased *m*-substitution which occurs when acetophenone is nitrated in the presence of an excess of concentrated sulphuric acid below 0° has already been observed by Rupe, Braun, and Zembruski (*Ber.*, 1901, **34**, 3522), who isolated 80—90% of pure *m*-nitroacetophenone under these conditions, whereas Camps (*Arch. Pharm.*, 1901, **240**, 1) found only 55% when the nitration was carried out in nitric acid (*d* 1·52) alone. Repetition of Camps's nitration shows that his value is too low, the actual figure being 70%. The anticipated increase in *m*-substitution when nitration is effected in the presence of a large excess of sulphuric acid is, however, clearly established by the results summarised in Table I, details of which are to be found in the experimental portion of this paper.

TABLE I.

Nitration of Ph·COR *under various conditions.*

Nitration No.	Conc. of sulphuric acid.	Density ($d^{15°}$) of nitric acid.	Mean proportion of *m*-isomeride formed (%), (a) without added Am_2SO_4.	(b) with added Am_2SO_4.
		R = H.		
1—2	7·3% free SO_3	1·53	90·8	85·9
3—4	5·0% "	"	89·0*	84·3
5	" "	"	—	85·0†
6	" "	"	—	86·1†
7—8	2·7% "	"	89·8	86·1
9—10	90%	"	86·5	83·2
11—12	80%	"	83·9	79·7
13	0%	"	72·1	—
		R = Me.		
14—15	7·3% free SO_3	1·53	90·0	83·6
16—17	80%	"	83·1	79·5
18	0%	"	69·8	—
19	"	1·505	68·1	—
20	"	1·485	66·9	—

* Flürscheim and Holmes (J., 1928, 2230) record only 78·65% obtained under similar, but not identical, nitration conditions.

† Rubidium sulphate used.

The proportion of the *m*-nitro-isomeride formed is greatest in sulphuric acid containing free sulphur trioxide, the presence of which will tend to preclude any hydrolysis of the oxonium salt. Such hydrolysis explains the decreasing proportion of *m*-nitration observed as the dilution of the sulphuric acid is increased. Even in nitric acid alone, a small but definite tendency towards the formation of the salt-like complex, postulated above, can be detected, since slight dilution of the nitric acid causes a corresponding small decrease in the proportion of the *m*-isomeride formed (Nos. 18—20).

In the experiments in concentrated sulphuric acid, evidence has been adduced that benzaldehyde and acetophenone *exist* largely in the form of oxonium salts in sulphuric acid solution. Proof that they *are nitrated* mainly through the kation of the salt is afforded by the observation (Table I) that *m*-substitution is depressed by the addition of ammonium sulphate in a manner exactly similar to that which had already been shown to occur in the case of the pseudo-base, benzylidene-*m*-nitroaniline (Baker and Ingold, *loc. cit.*). It is difficult, therefore, to escape the conclusion that the similar depression observed in the case of the carbonyl compounds is due to the same cause, *viz.*, the depression of the ionic dissociation,

$$\mathrm{Ph{\cdot}\overbrace{CR{:}OH}^{\oplus} + \overset{\ominus}{H}SO_4 \rightleftharpoons Ph{\cdot}\overbrace{CR{:}OH}^{\oplus}\Big\}\overset{\ominus}{H}SO_4 \rightleftharpoons Ph{\cdot}COR + H_2SO_4},$$

and subsequent conversion of the undissociated salt either into the pseudo-salt $\mathrm{Ph{\cdot}CR(OH)(HSO_4)}$ or into the free carbonyl compound and sulphuric acid.

In order to ensure that the results are not due to any interaction between the ammonium sulphate and benzaldehyde, *e.g.*, $\mathrm{Ph{\cdot}CH{:}O} + \mathrm{(NH_4)HSO_4} \longrightarrow \mathrm{Ph{\cdot}\overbrace{CH{:}NH_2}^{\oplus}\Big\}\overset{\ominus}{H}SO_4 + H_2O}$, giving the salt of a Schiff's base, the experiments were repeated (Nos. 5—6) with rubidium sulphate, with essentially the same results.

These results, together with those previously recorded (Baker and Ingold, *loc. cit.*), show that the proportion of the *m*-nitro-isomeride (72%) formed in the nitration of benzaldehyde in nitric acid alone (No. 13) may be diminished to 41% by nitration with acetyl nitrate [where nitration occurs mainly through the diacetate, $\mathrm{Ph{\cdot}CH(OAc)_2}$] or increased to 90% by addition of fuming sulphuric acid to the nitric acid (nitration through the oxonium salt), and thus indicate the lines along which the proportions of *op*- and *m*-substitution may be controlled at will by variation of the conditions of nitration.

EXPERIMENTAL.

Samples of benzaldehyde and acetophenone purified as described in Part I (preceding paper) were used.

Nitration of Benzaldehyde and Acetophenone in the Presence of Sulphuric Acid.—In all cases the carbonyl compound was added slowly with mechanical stirring to the nitration mixture, the temperature being kept at 5° ± 1° for about 2 hours. The solution was then allowed to attain the ordinary temperature, at which it was kept for a further 24 hours. It was then poured on an excess of potassium hydrogen carbonate and ice, and the neutral products were extracted with benzene or ether. The last traces of solvent were removed from the residue from the dried extract by desiccation in a vacuum to constant weight. In most cases the yield of mononitro-derivatives was about 90%, and in several representative experiments it was shown that the small loss of material was accounted for by the acid products formed by slight oxidation during the nitration. The numerical details, except analyses, relating to these nitrations are recorded in Table II.

Nitration of Benzaldehyde and Acetophenone in Nitric Acid alone.—The carbonyl compound was added slowly at − 8° to − 10°, with mechanical stirring, to the nitric acid, the density (at 15°) of which was determined approximately with a hydrometer. The mixture was left at this temperature for about 1 hour, and then poured on crushed ice and potassium hydrogen carbonate, and worked up in a manner similar to that described above. Nitration No. 18 was carried out under the conditions used by Camps (*loc. cit.*). The numerical data are recorded in Table III.

TABLE II.

Nitration No.	Wt. of Ph·COR taken (g.).	HNO_3 ($d^{15°}$ 1·53), (g.).	Wt. of H_2SO_4 (g.).	Conc. of H_2SO_4.	Wt. of Am_2SO_4 added (g.).	Product (g.),	
						neutral.	acid.
			Benzaldehyde (R = H).				
1	2·922	3	31	7·3% free SO_3	0	3·576	0·276
2	3·048	3	31	,,	6	3·781	0·475
3	2·998	3	45	5·0% free SO_3	0	3·858	0·227
4	3·014	3	45	,,	9	3·839	0·352
5	1·030	1·5	17	,,	7*	0·995	—
6	2·022	2	30	,,	7·5*	2·579	—
7	2·968	3	60	2·7% free SO_3	0	3·809	0·262
8	2·964	3	60	,,	15	3·868	0·384
9	2·994	3	60	90%	0	3·518	0·411
10	2·981	3	60	,,	12	3·686	0·327
11	2·959	3	60	80%	0	3·464	—
12	3·201	3	60	,,	12	3·815	—
13	3·520	25	0	—	0	4·801	—
			Acetophenone (R = Me).				
14	3·406	3	31	7·3% free SO_3	0	2·798	—
15	3·410	3	31	,,	6	3·284†	—
16	3·215	3	60	80%	0	2·611	—
17	3·013	3	60	,,	12	2·765	—

* Rubidium sulphate used. † Some mechanical loss.

Determination of the Proportion of Isomerides formed.—This was effected by oxidation of a weighed portion of the neutral product with boiling alkaline potassium permanganate, and analysis of the resulting mixed nitrobenzoic acids by the method of Flürscheim and Holmes (J., 1928, 448) in the usual manner. The results are recorded in Table IV.

TABLE III.

Nitration No.	Ph·COMe taken (g.).	HNO_3 (g.).	Density of HNO_3 ($d^{15°}$).	Temp.	Time (hrs.).	Neutral product (g.).
18	2·485	25	1·53	− 8°	0·8	3·431
19	3·062	25	1·505	− 8	1·25	4·003
20	2·305	25	1·485	− 8	1·5	2·401

TABLE IV.

				Recovered (g.).			Composition of acids. R·CO₂H (mols. %) R =			Percentage of nitro-isomerides,	
Nitration No.	Neutral product oxidised (g.).	Acids obtained (g.).	Separated (g.).	$C_6H_5{\cdot}CO_2H$.	$C_6H_2Br_3{\cdot}NH_2$.	$C_6HBr_3{<}^{NH_2}_{CO_2H}$.	C_6H_5.	*op*- $NO_2{\cdot}C_6H_4$.	*m*- $NO_2{\cdot}C_6H_4$.	*op*-.	*m*-.
1	2·131	2·288	1·055	0·010	0·183	2·016	1·3	9·2	89·5	9·3	90·7
			0·690	0·010	0·116	1·322	2·0	8·9	89·1	9·0	91·0
2	2·049	2·205	0·811	0·020	0·216	1·442	3·5	14·1	82·4	14·5	85·5
			0·723	0·013	0·178	1·263	2·5	13·4	84·1	13·8	86·2
3	1·997	2·146	0·468	0·007	0·101	0·897	2·1	11·1	86·8	11·3	88·7
			0·689	0·006	0·141	1·307	1·2	10·7	88·1	10·8	89·2
4	2·002	2·121	0·654	0·011	0·201	1·168	1·7	16·2	82·1	16·3	83·7
			0·643	0·008	0·182	1·156	1·7	14·9	83·4	15·1	84·9
5	0·995	1·037	0·427	0·023	0·112	0·721	7·7	13·9	78·4	15·0	85·0
6	2·327	2·202	1·012	0·057	0·233	1·652	8·3	12·6	79·1	13·9	86·1
7	2·256	2·332	1·034	0·012	0·200	1·944	1·7	10·3	88·0	10·4	89·6
			0·708	0·008	0·134	1·359	1·6	9·9	88·5	10·0	90·0
8	2·473	2·407	0·928	0·029	0·235	1·681	4·3	13·1	82·5	13·7	86·3
			0·746	0·021	0·195	1·343	4·0	13·5	82·5	14·1	85·9
9	2·002	2·046	0·451	0·011	0·121	0·837	3·3	13·6	83·1	13·9	86·1
			0·747	0·014	0·188	1·385	2·6	13·0	84·4	13·2	86·8
10	2·000	2·042	0·768	0·010	0·236	1·341	1·8	16·4	81·8	16·7	83·3
			0·859	0·008	0·274	1·504	1·3	16·9	81·8	16·9	83·1
11	2·063	2·157	0·850	0·007	0·250	1·477	1·2	15·9	82·9	16·1	83·9
12	2·487	2·565	0·907	0·024	0·340	1·514	3·7	19·6	76·7	20·3	79·7
13	2·824	2·540	0·767	0·020	0·383	1·121	3·8	26·8	69·4	27·9	72·1
14	1·936	1·057*	0·660	0·074	0·110	1·098	15·6	8·6	75·8	10·0	90·0
15	2·100	1·413	0·594	0·014	0·169	0·968	3·6	15·9	80·5	16·4	83·6
16	1·988	1·733	0·870	0·054	0·238	1·338	9·3	15·2	75·5	16·9	83·1
17	1·639	1·193	0·829	0·263	0·193	0·847	43·0	11·7	45·3	20·5	79·5
18	2·544	2·009	0·991	0·024	0·475	1·263	3·9	28·6	67·5	29·9	70·1
			0·884	0·028	0·465	1·192	4·7	29·1	66·2	30·5	69·5
19	2·679	1·691	0·800	0·044	0·450	1·081	7·8	29·6	62·6	31·9	68·1
20	1·934	1·750	0·886	0·431	0·241	0·553	61·5	12·7	25·8	33·1	66·9

* Mechanical loss.

We wish to thank the Research Fund Committee of the Chemical Society for a grant by the aid of which some of the expense incurred in this investigation has been met.

THE UNIVERSITY, LEEDS. [*Received, December 2nd,* 1930.]