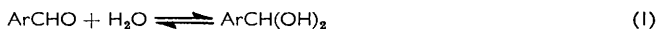


305. *Oxidations of Organic Compounds by Cobaltic Salts.*
*Part III.*¹ *The Oxidation of Aromatic Aldehydes.*

By T. A. COOPER and WILLIAM A. WATERS.

The kinetics of the oxidations of *m*- and *p*-nitrobenzaldehydes, piperonal and veratraldehyde, by cobaltic perchlorate, have been examined in methyl cyanide-water at 10°. The reaction velocity is of the first order with respect to both [Aldehyde] and [Cobalt(III)] and shows an inverse acidity dependence. A kinetic isotope effect of 2.3 was found for the oxidation of *m*-nitrobenzaldehyde, showing that the fission of the C-H (C-D) bond of the aldehyde group is involved in the rate-determining process. Piperonal and veratraldehyde probably oxidise by attack on the ether function.

PREVIOUS investigations in this laboratory have shown that only those aldehydes which can form enols are rapidly attacked by one-electron oxidants of moderate redox potential.² The much slower oxidations of formaldehyde³ and of chloral⁴ involve the hydrates, H₂C(OH)₂ and Cl₃C·CH(OH)₂, which behave like alcohols towards such oxidants. Cobaltic ions, however, have a sufficiently high redox potential to be able to attack even aromatic aldehydes, for which hydration



is not a favoured equilibrium, and yield the corresponding acids. The mechanism of this oxidation thus merits special investigation.

The direct attack on benzaldehyde by cobaltic acetate in acetic acid-sulphuric acid has been examined briefly by Bawn and Jolley⁵ as part of a detailed study of the catalysis

¹ Part II, Hoare and Waters, *J.*, 1962, 971.

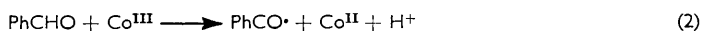
² Waters, "Homolytic Oxidation Processes," "Progress in Organic Chemistry," Butterworths, London 1961, Vol. 5, p. 1.

³ Kemp and Waters, *Proc. Roy. Soc.*, 1963, *A*, 274, 480.

⁴ Drummond and Waters, *J.*, 1953, 441; Littler and Waters, *J.*, 1959, 1300.

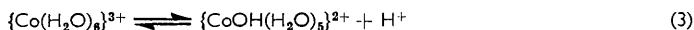
⁵ Bawn and Jolley, *Proc. Roy. Soc.*, 1956, *A*, 237, 313.

of the autoxidation of benzaldehyde by cobaltous salts. Their kinetic studies led to the conclusion that in glacial acetic solution the initial radical-forming process of the autoxidation is the direct oxidation of benzaldehyde to benzoyl radicals by cobaltic ions:



Their few measurements indicated that the reaction is of the first order with respect to both benzaldehyde and cobalt(III).

The direct oxidation of aromatic aldehydes by cobaltic salts clearly needs much more detailed study, since the reactivity of cobalt(III) depends markedly upon the nature of the attached ligand groups, through which one electron must be abstracted from the organic substrate and eventually picked up by the cobalt. Thus in aqueous solution the reactivity of cobalt(III) is governed by the equilibrium:^{6,7}



when complexing anions such as sulphate are absent. In this way the inverse acidity dependence found for oxidations by cobaltic perchlorate solutions can be explained.

Aromatic aldehydes are so insoluble in water that a mixed solvent had to be used, but fortunately other work in this laboratory⁸ had shown that methyl cyanide-water mixtures could be employed provided that the methyl cyanide had itself been rigorously purified. It had been found with this binary solvent that, in mixtures of up to 60% by volume of methyl cyanide, reaction velocities change systematically with solvent composition, according to the equation:

$$\log k_{\text{solvent}}/\log k_{\text{water}} = \text{Const. (\% methyl cyanide)} \quad (4)$$

This holds for both *m*- and *p*-nitrobenzaldehydes, which were finally selected as substrates for detailed kinetic study, since unlike benzaldehyde, they are not prone to autoxidation in solution: Table 1 lists our confirmatory evidence. Good first-order plots for the consumption of cobaltic perchlorate over 2–3 half-lives were obtained when the oxidant was treated with a five-fold or greater molar excess of either aldehyde. Table 2 shows that the oxidations are of the first order with respect to the aldehydes. The acidity dependence of the oxidation of *p*-nitrobenzaldehyde is shown in Table 3; in accordance with equilibrium (3) the rate decreases as the acid becomes more concentrated. The second-order rate constant for the oxidation of *p*-nitrobenzaldehyde was independent of the ionic strength (Table 4*a*) and decreased by only 13% for a 100% increase in the concentration of cobaltous ions in the system (Table 4*b*).

The dependence of the rate of oxidation of each aldehyde on the reaction temperature (Table 5) gives the values for the energies and entropies of activation:

	E_a (kcal. mole ⁻¹)	ΔS (e.u.)
<i>p</i> -Nitrobenzaldehyde	20.7	+ 13.1
<i>m</i> -Nitrobenzaldehyde	21.3	+ 14.1

It was found possible to prepare the deuterated aldehyde, *m*-NO₂·C₆H₄·CDO (but not the para-compound), by reduction of ethyl nitrobenzoate to the corresponding alcohol with lithium aluminium deuteride, and subsequent oxidation to the aldehyde with *t*-butyl chromate⁹ and pyridine as catalyst.¹⁰ Table 2*c* shows that for the oxidations of the proto- and deuterio-compounds there is a primary kinetic isotope effect of 2.3 at 10°. Consequently, fission of the aldehydic C–H bond is involved in the rate-determining step of these oxidations.

⁶ Part I, Hoare and Waters, *J.*, 1962, 965.

⁷ Shankar and de Souza, *J. Inorg. Nuclear Chem.*, 1962, **24**, 693.

⁸ Hoare and Waters, Part IV, *J.*, in the press.

⁹ Oppenauer and Oberrauch, *Anales. Asoc. quim. argentina*, 1949, **37**, 246.

¹⁰ Leo and Westheimer, *J. Amer. Chem. Soc.*, 1952, **74**, 4383.

TABLE 1.

(a) Influence of solvent composition on rate of oxidation of *p*-nitrobenzaldehyde.
Initial Co^{III} ca. 10^{-2}M ; Co^{II} ca. 0.03M ; HClO_4 1.65M ; Ionic strength 1.75M ; Temp. 10° .

% MeCN (by vol.)	45.0	45.0	45.0	35.8	29.6	25.9	22.2	18.5	14.8	11.2	7.42
k_2 (l. mole $^{-1}$ sec. $^{-1}$)	0.131	0.138	0.103	0.0928	0.0852	0.0781					

(b) Influence of solvent composition on rate of oxidation of *m*-nitrobenzaldehyde; conditions as (a).

% MeCN (by vol.)	45.0	45.0	35.8	29.6	25.9	22.2	18.5	14.8	11.2	7.42
$10^2 k_2$	7.39	7.50	6.11	5.48	5.21	4.93	4.69	4.44	4.10	3.84

TABLE 2.

(a) Order of reaction with respect to *p*-nitrobenzaldehyde.
Initial $[\text{Co}^{\text{III}}]$ ca. 10^{-2}M ; $[\text{Co}^{\text{II}}]$ ca. 0.03M ; $[\text{HClO}_4]$ 1.65M ; Ionic strength 1.75M ; 45% MeCN by volume; Temp. 10° .

10^2 [Aldehyde] (M)	4.66	6.35	6.62	8.05	8.34	10.16	10.86	12.39	13.24	14.10	15.14
$10^2 k'$ (sec. $^{-1}$)	0.618	0.808	0.818	1.02	1.11	1.32	1.49	1.62	1.67	1.91	2.06
k_2 (l. mole $^{-1}$ sec. $^{-1}$)	0.133	0.127	0.123	0.127	0.133	0.130	0.137	0.131	0.126	0.135	0.136

Mean value of $k_2 = 0.131 \pm 0.006$ l. mole $^{-1}$ sec. $^{-1}$.

(b) Reaction velocity and kinetic isotope effect for *m*-nitrobenzaldehyde; conditions as (a).

	<i>m</i> -Nitrobenzaldehyde.										
10^2 [Aldehyde] (M)	3.79	5.75	6.63	7.66	8.58	10.8	11.5	13.3	14.4	15.7	
$10^2 k'$ (sec. $^{-1}$)	2.94	4.15	4.80	5.90	6.04	8.36	8.48	9.91	10.1	11.5	
	Calc. $k_2 = 7.4 \pm 0.4 \times 10^{-2}$ l. mole $^{-1}$ sec. $^{-1}$.										
	<i>Deutero-m-nitrobenzaldehyde.</i>										
10^2 [Aldehyde] (M)	4.07	6.06	8.68	11.0	13.7	16.1					
$10^2 k'$ (sec. $^{-1}$)	1.22	1.91	2.88	3.82	4.54	4.82					
	Calc. $k_2 = 3.2 \pm 0.2 \times 10^{-2}$ l. mole $^{-1}$ sec. $^{-1}$.										

Hence $k_{\text{H}}/k_{\text{D}} = 2.3$ at 10° , which corresponds to ΔE_a of 464 cal. mole $^{-1}$.

TABLE 3.

Influence of acid concentration on the rate of oxidation of *p*-nitrobenzaldehyde.
Initial $[\text{Co}^{\text{III}}]$ ca. 10^{-2}M ; $[\text{Co}^{\text{II}}]$ ca. 0.03M ; 45% MeCN; Temp. 10° ; Ionic strength 3.50M .

$[\text{HClO}_4]$ (M)	0.831	1.163	1.386	1.622	1.839	2.286	2.734	3.183	3.406
$10k_2$ (l. mole $^{-1}$ sec. $^{-1}$)	2.84	2.06	1.59	1.31	1.13	0.881	0.617	0.508	0.492
$(k_2 + 0.03)$ $[\text{HClO}_4]$ (sec. $^{-1}$)	0.261	0.274	0.262	0.261	0.263	0.270	0.250	0.257	0.269

TABLE 4.

(a) Influence of ionic strength on rate of oxidation of *p*-nitrobenzaldehyde.
Initial $[\text{Co}^{\text{III}}]$ ca. 10^{-2}M ; $[\text{Co}^{\text{II}}]$ ca. 0.03M ; $[\text{HClO}_4]$ 0.833M ; 45% MeCN; Temp. 10° .

Ionic strength (M)	0.93	1.12	1.35	1.60	1.83	2.06	2.28	2.50	2.72	3.22	3.50
k_2 (l. mole $^{-1}$ sec. $^{-1}$)	0.29	0.32	0.27	0.31	0.28	0.27	0.30	0.26	0.30	0.27	0.30

(b) Influence of concentration of cobaltous perchlorate on the rate of oxidation of *p*-nitrobenzaldehyde.
Initial $[\text{Co}^{\text{III}}]$ ca. 10^{-2}M ; 45% MeCN; Temp. 10° ; Ionic strength ca. 1.75M .

$10^2 \times [\text{Co}^{\text{II}}]$ (M)	3.07	3.43	4.34	5.25	6.16
k_2 $[\text{HClO}_4]$ (sec. $^{-1}$)	0.264	0.253	0.245	0.235	0.229

The oxidations of benzaldehyde and *p*-chlorobenzaldehyde did not give consistent results due to the effects of oxygen, which could not be removed completely from the cobaltic perchlorate solutions because of their self-decomposition:

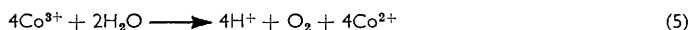


TABLE 5.

(a) Influence of temperature of reaction on the rate of oxidation of *p*-nitrobenzaldehyde
Initial [Co^{III}] *ca.* 10⁻²M; [Co^{II}] *ca.* 0.03M; [HClO₄] 1.65M; 45% MeCN; Ionic strength 1.75M.
Temp. 27.1° 24.3° 20.2° 20.3° 15.7° 10.9° 10.0° 5.0°
10³*k*₂ (l. mole⁻¹ sec.⁻¹) 10.96 7.90 4.89 5.06 2.85 1.52 1.30 0.706
Hence *E*_a = 20.7 kcal. mole⁻¹, Δ*H*† = 20.1 kcal. mole⁻¹, Δ*G*† = 16.4 kcal. mole⁻¹; Δ*S*† = 13.1 e.u.

(b) Influence of temperature of reaction on rate of oxidation of *m*-nitrobenzaldehyde;
conditions as (a) above.
Temp. 27.2° 24.3° 20.1° 15.7° 10.9° 10.0° 5.5°
10³*k*₂ (l. mole⁻¹ sec.⁻¹) 6.90 5.09 2.93 1.74 0.899 0.738 0.422
Hence *E*_a = 21.3 kcal. mole⁻¹, Δ*H*† = 20.7 kcal. mole⁻¹, Δ*G*† = 16.7 kcal. mole⁻¹; Δ*S*† = 14.1 e.u.

TABLE 6.

(a) Order of reaction with respect to piperonal.
Initial [Co^{III}] *ca.* 0.005M; [Co^{II}] *ca.* 0.03M; 45% MeCN; [HClO₄] 1.65M; Ionic strength 1.75M;
Temp. 10°.

10 ² × [Piperonal] (M) ...	0.711	0.956	1.23	1.42	1.51	1.72	1.91	2.18
10 ³ <i>k</i> ' (sec. ⁻¹)	1.87	2.30	3.27	3.75	4.22	4.70	4.98	5.50
<i>k</i> ₂ (l. mole ⁻¹ sec. ⁻¹)	2.63	2.40	2.66	2.64	2.79	2.73	2.63	2.52
Mean value of <i>k</i> ₂ = 2.6 l. mole ⁻¹ sec. ⁻¹ .								

(b) Order of reaction with respect to veratraldehyde. Conditions as (a) above.

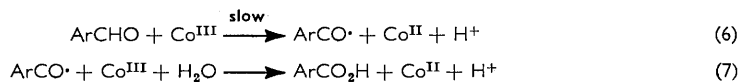
10 ² × [Veratraldehyde] (M)	0.691	0.759	0.915	1.20	1.34	1.54	1.56
10 ³ <i>k</i> ' (sec. ⁻¹)	1.65	1.70	2.06	2.86	3.24	3.71	3.73
<i>k</i> ₂ (l. mole ⁻¹ sec. ⁻¹)	2.39	2.24	2.25	2.38	2.42	2.41	2.39
Mean value of <i>k</i> ₂ = 2.3 ₈ l. mole ⁻¹ sec. ⁻¹ .							

Both these substrates oxidised more slowly than the nitro-aldehydes, and their second-order rate constants were of the order of 10⁻² l. mole⁻¹ sec.⁻¹. In each case oxygen accelerated the rate of oxidation.

No oxygen effect was found for the oxidations of piperonal and veratraldehyde, but the oxidised solutions were bright yellow, in contrast to the pale pink solutions obtained from the reactions of the other substrates. Both piperonal and veratraldehyde oxidised at rates about twenty times the rate of oxidation of *p*-nitrobenzaldehyde (Table 6). Some qualitative tests of the reaction of cobaltic perchlorate with 1,3-benzodioxole showed exactly similar behaviour, and so it is probable that in these cases the oxidant attacks the ether functions and not the aldehyde groups. The behaviour of these substances closely resembles that found by Adler and his colleagues^{11,12} for the periodate oxidation of phenolic ethers.

DISCUSSION

The oxidations of *m*- and *p*-nitrobenzaldehyde, like that of benzaldehyde itself, are evidently to be represented as direct oxidation of the aldehyde group:



Reaction (6) thus involves removal of one electron from the organic molecule. This occurs more rapidly with the nitro-substituted aldehydes than with benzaldehyde, although nitro-groups are electrophilic and might be expected to hinder such electron removal. The greater reactivity of the nitro-compounds can reasonably be ascribed to the greater degree of resonance stabilisation of the radical NO₂·C₆H₄·CO· than of C₆H₅·CO·.

Equation (6) correctly represents the oxidation process which occurs, but it gives no

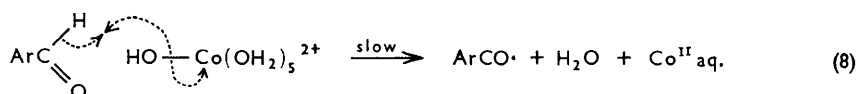
¹¹ Adler and Magnusson, *Acta Chem. Scand.*, 1959, **13**, 505.

¹² Adler, Falkehag, and Smith, *Acta Chem. Scand.*, 1962, **16**, 529.

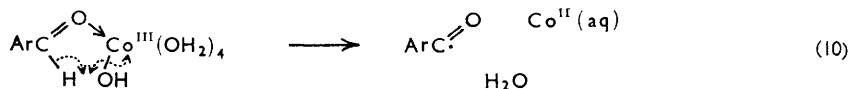
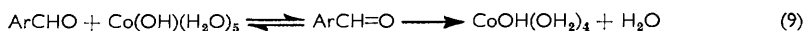
1542 Oxidations of Organic Compounds by Cobaltic Salts. Part III.

indication of the way in which the homolysis of the C-H bond is effected. To explain the course of the oxidative step, two alternative mechanisms can be suggested, both of which could be consistent with the observed positive entropies of activation.¹³

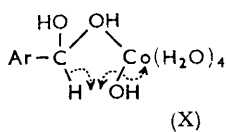
(A) Removal of a hydrogen atom through an attached ligand group (-OH), of the cobaltic ion.



(B) Oxidation following ligand displacement and formation of an aldehyde-cobalt complex.



A possible variant of this involves the formation of the hydrated aldehyde, $\text{ArCH}(\text{OH})_2$, which might co-ordinate as an alcohol, *e.g.*, X, but there is no evidence to indicate the need for the initial hydration of an aromatic aldehyde before it becomes prone to attack by any oxidant.



The relative merits of both outer sphere (*i.e.*, A), and inner sphere (*i.e.*, B) mechanism for the electron-transfer reactions of the transition metals have been discussed by several workers.¹⁴ From our results either route seems equally plausible for the present oxidations.

EXPERIMENTAL

Materials.—Cobaltic perchlorate solutions were prepared as described in Part I.⁶ Technical methyl cyanide (500 ml.) (for impurities see Coetzee *et al.*¹⁵), was purified by adding concentrated sulphuric (60 ml.) cautiously, with cooling, and then potassium permanganate (65 g.) in portions. The liquid, which boiled spontaneously, was refluxed for 3 hr., filtered, dried (K_2CO_3), and refluxed twice (P_2O_5) for 3 hr. The methyl cyanide was then fractionated from fresh phosphorus pentoxide, collected at 81.5° , freed from oxygen, and stored under nitrogen. It was found to be spectroscopically pure.

The mixed solvent was prepared by using water which had been re-distilled from alkaline permanganate, purged with nitrogen, and stored under nitrogen. Benzaldehyde was purified as described by Waters and Wickham-Jones.¹⁶ *m*- and *p*-Nitrobenzaldehyde were recrystallised to constant m. p. *p*-Chlorobenzaldehyde, piperonal, and veratraldehyde were sublimed under reduced pressure to constant m. p.

Deutero-*m*-nitrobenzaldehyde. A suspension of lithium aluminium deuteride (1.4 g.; 96.7%; from Metal Hydrides Inc., N.Y.), in dry ether (270 ml.), was added slowly to a solution of ethyl *m*-nitrobenzoate (10 g.) in dry ether (240 ml.), under nitrogen. The mixture was stirred at room temperature for 3 hr., treated with ethyl acetate, and acidified. The ethereal layer was separated, dried (MgSO_4), and fractionated. The dideutero-*m*-nitrobenzyl alcohol was collected at $170\text{--}175^\circ/10$ mm. It froze to a pale yellow solid, m. p. $26\text{--}28^\circ$ (51%). A red liquid, probably 3,3'-di(hydroxymethyl)azobenzene, remained, but pyrolysed slowly during the fractionation.

The dideutero-*m*-nitrobenzyl alcohol (5 g.) was dissolved in benzene (18 ml.) to which a few drops of pyridine had been added, and oxidised at room temperature with a solution of chromium trioxide (4.2 g.) in *t*-butyl alcohol (9 g.). After 12 hr. hydrazine sulphate was added, the

¹³ Schaleger and Long, "Entropies of Activation and Mechanisms of Reactions in Solution," in "Advances in Physical Organic Chemistry," Academic Press, New York, Vol. 1, 1963; Kohnstam, *Chem. Soc. Special Publ. No. 16*, p. 179.

¹⁴ See *Discuss. Faraday Soc.*, **29**, 1960.

¹⁵ Coetzee, Cunningham, McGuire, and Padmanabhan, *Analyt. Chem.*, 1962, **34**, 1139.

¹⁶ Waters and Wickham-Jones, *J.*, 1951, 812.

mixture diluted with ether, warmed, filtered, dried (MgSO_4), and evaporated. The dark residue was repeatedly sublimed at 15 mm. pressure and yielded white feathery crystals (53% ; overall yield from the ester, 27%), m. p. 57.5° . The product showed infrared spectral peaks indicative of C-D stretching at 2120 and 2075 cm^{-1} , whilst the proto-compound showed peaks at 2840 and 2735 cm^{-1} (Found: 20.4 atoms-% of deuterium, *i.e.*, 100% deuteration).

m-Nitrobenzaldehyde. This was prepared similarly from ethyl *m*-nitrobenzoate. It had the same m. p. as the deuterio-compound, and both specimens formed a 2,4-dinitrophenyl-hydrazone which decomposed at 294° . The synthetic proto-compound was oxidised by cobaltic perchlorate at the same rate as was the purified technical material.

The preparation of *p*-nitrobenzyl alcohol by an analogous route to that used for the *meta*-compound was unsuccessful (compare Felkin¹⁷): an intractable mixture of insoluble materials was obtained.

Kinetics.—The experimental techniques used were those described in Part I,⁶ but because of the large absorption by aromatic aldehydes in the ultraviolet spectrum, the disappearance of the cobaltic ions had to be followed at 594 $\text{m}\mu$. The weakness of the absorption at this wavelength necessitated the use of 10-mm. glass-stoppered cells, and initial concentrations of cobaltic perchlorate of approximately 10^{-2}M . The spontaneous decomposition of the cobaltic perchlorate was appreciable at lower acidities (under 1M), but was negligible at the higher acidity (1.65M) generally employed for these kinetic studies.

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[Received, July 9th, 1963.]

¹⁷ Felkin, *Compt. rend.*, 1950, **280**, 304.
