235. *The Oxidation of* iso*Butyraldehyde with the Free Radical,* $\cdot O{\cdot}N(SO_3K)_2$, *from Potassium Nitrosyldisulphonate.*

By G. D. Allen and William A. Waters.

The oxidation of *iso*butyraldehyde by the free radical $\cdot O{\cdot}N(SO_3K)_2$, like that of oxidations by other 1-electron abstracting agents, occurs by electron removal from the enol anion: α-hydroxy*iso*butyraldehyde is the first product.

Potassium nitrosyldisulphonate (Frémy's salt), which in aqueous solution is completely dissociated into the purple free radical $\cdot O{\cdot}N(SO_3K)_2$, has recently been used for the oxidation of phenols and aromatic amines,[1] but its reactions with aliphatic molecules do not appear to have been studied. Since it should be a 1-electron abstracting reagent it was expected that it would resemble potassium ferricyanide and oxidise aliphatic aldehydes and ketones in alkaline solution by attacking them in the forms of their enol anions.[2]

If carefully prepared, Frémy's salt gives deep purple solutions, reasonably stable [3] in the pH range 8—11, which can easily be analysed colorimetrically as their absorptions in the 545 mμ region are directly proportional to their concentrations as measured both by weighing of the orange dimeric solid and by iodine–thiosulphate titration. Solutions in which some decomposition has occurred can still be estimated colorimetrically, though not titrimetrically since hydrolysis products then interfere.

Preliminary tests showed that aliphatic aldehydes were oxidised at measurable speeds in alkaline carbonate solutions at 25° whereas oxidation of ketones and nitro-paraffins required more strongly alkaline conditions under which some self-decomposition of the purple free radical occurred. The kinetics of the oxidation of *iso*butyraldehyde have consequently been studied in carbonate–bicarbonate buffers. The experimental results, which are collected in the Tables and the Figure, show that in buffers of constant ionic strength the initial rate of decolorisation of the free radical is a first-order process with respect to the radical itself, to *iso*butyraldehyde, and, approximately, to hydroxyl ion. This oxidation occurs at about a tenth of the rate of oxidation of *iso*butyraldehyde by alkaline ferricyanide (which is a zero-order process with respect to the oxidant [2]) and it can therefore be concluded that the rate-determining stage is that of electron abstraction from the enol anion (reaction 2).

$$\text{(1)}\quad Me_2CH{\cdot}CHO + OH^- \underset{\text{maintained}}{\overset{\text{Equilm.}}{\rightleftharpoons}} Me_2{:}CH{\cdot}O^- + H_2O$$

$$\text{(2)}\quad Me_2C{:}CH{\cdot}O^- + \cdot ON(SO_3K)_2 \xrightarrow{\text{Slow}} \{{:}O{\cdot}N(SO_3K)_2\}^- + Me_2\dot{C}{\cdot}CHO \underset{\text{Mesomeric}}{\longleftrightarrow} Me_2C{:}CH{\cdot}O\cdot$$

$$\text{(3)}\quad Me_2\dot{C}{\cdot}CHO + \cdot O{\cdot}N(SO_3K)_2 + H_2O \xrightarrow{\text{Fast}} Me_2C(OH){\cdot}CHO + HO{\cdot}N(SO_3K)_2$$

Though the colorimetric measurements showed that the rate of radical destruction increased in the later stages of the oxidation (see Figure), as would be the case if the primary

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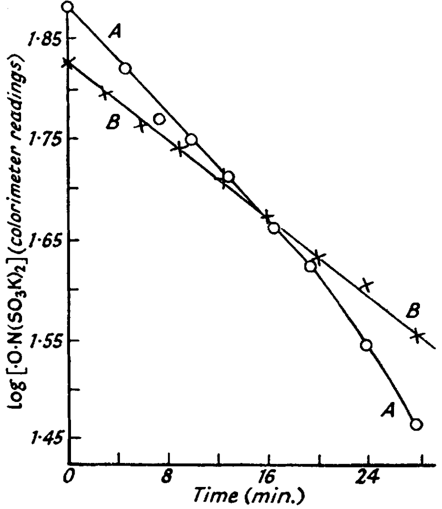
[1] Teuber *et al.*, *Chem. Ber.*, 1952, **85**, 95; 1953, **86**, 1036; 1954, **87**, 1236, 1252.
[2] Speakman and Waters, *J.*, 1955, 40.
[3] Murib and Ritter, *J. Amer. Chem. Soc.*, 1952, **74**, 3394; Li and Ritter, *ibid.*, 1953, **75**, 3024, 5823, 5828, 5831.

product underwent further oxidation, it was possible to show that after reaction mixtures gave positive qualitative tests for α-hydroxy*iso*butyraldehyde.[4] From the mixture of 2 : 4-dinitrophenylhydrazones obtained from such oxidised solutions that of α-methylacraldehyde, $CH_2{:}CMe{\cdot}CHO$, the dehydration product of α-hydroxy*iso*butyraldehyde, was



A, No added salt.
B, $NaClO_4$ *added.*

TABLE 1. *Oxidation of* iso*butyraldehyde with the radical* $\cdot O\cdot N(SO_3K)_2$ *at* 25° *and* pH 9·63.

Initial aldehyde concn. = 6·44 × 10^{-2}M.

Time (min.)	[Radical] (10^{-3}M)	Log_{10} [Radical]	10^2k_{uni}	Time (min.)	[Radical] (10^{-3}M)	Log_{10} [Radical]	10^2k_{uni}
0·0	9·10	$\bar{3}$·9590	3·11	24·0	3·93	$\bar{3}$·5944	3·34
2·0	8·55	$\bar{3}$·9320	3·73	27·5	3·60	$\bar{3}$·5563	3·37
4·5	7·71	$\bar{3}$·8871	2·97	31·5	3·20	$\bar{3}$·5051	3·32
9·5	6·96	$\bar{3}$·8426	3·29	34·3	2·80	$\bar{3}$·4472	3·43
12·3	6·06	$\bar{3}$·7825	3·34	41·3	2·53	$\bar{3}$·4031	3·11
15·0	5·52	$\bar{3}$·7419	3·35	44·3	2·28	$\bar{3}$·3579	3·36
18·0	5·17	$\bar{3}$·7139	3·13	47·3	1·73	$\bar{3}$·2380	3·46
21·5	4·46	$\bar{3}$·6493	3·32				

Mean k_{uni} = 3·31 × 10^{-2} min.$^{-1}$.

TABLE 2. *Velocity of oxidation of* iso*butyraldehyde by the free radical* $\cdot O\cdot N(SO_3K)_2$ *at* 25°.

pH	[OH⁻] (10^{-5}M)	10^2k_{uni} (min.$^{-1}$)	No. of obsns.	[Aldehyde] (10^{-2}M)	k/[Aldehyde]	Mean	$10^{-3}k$/[Ald.][OH⁻]
10·65	44·7	4·44	7	1·46	3·04	3·08	6·89
		5·45	5	1·75	3·11		
		5·43	6	1·75	3·10		
10·36	22·9	7·20	5	4·54	1·58	1·57	6·86
		4·37	6	2·77	1·57		
10·18	15·1	1·72	6	1·72	1·00	1·03	6·82
		1·84	5	1·72	1·06		
		4·21	6	4·10	1·02		
9·95	8·91	1·29	8	1·44	0·90	0·86	9·6
		2·88	6	3·55	0·81		
		6·23	4	7·09	0·88		
		7·36	4	8·78	0·84		
9·63	4·27	1·92	6	3·45	0·56	0·55	12·9
		3·06	8	5·17	0·59		
		3·31	14	6·44	0·51		
		5·04	5	8·62	0·58		

In all kinetic experiments the aldehyde concentration was greatly in excess of that of the free radical. Concentrations were measured for 50—70% disappearance of the latter.

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[4] Conant and Aston, *J. Amer. Chem. Soc.*, 1928, **50**, 2783.

separated, confirming the view that the free-radical oxidation of aliphatic aldehydes occurs at the carbon atom adjacent to the aldehyde group.

The Figure shows that the rate of oxidation is significantly reduced by the addition of the neutral salt potassium perchlorate. Addition of sodium chloride produced a similar effect. Since the oxidation stages given above are reactions between ions of similar sign, $Me_2CH\!:\!CH\cdot O^-$ and $\{\cdot ON(SO_3)_2\}^{2-}$, or between anions and neutral molecules, with which a positive salt effect would be expected, we would point out that the ionic strength of the buffer solution (0·4M) was always very much greater than that of the reactants (10^{-2} to 10^{-3}M) and suggest that at this very high ionic strength the neutral salt may be acting by diminishing the overall basicity of the medium. Enolisation of aldehydes is, after all, a process controlled by general base catalysis and the value of $[OH^-]$ indicated by glass electrode measurements (always subject to instrumental errors on the alkaline side) may not be quite the true function for use in representing quantitatively the equilibrium represented by reaction (1) above.

Kinetic measurements have also been carried out with propaldehyde, with a similar but less decisive outcome. The initial stage of the oxidation is again a first-order process with respect to the $\cdot O\cdot N(SO_3K)_2$ radical, is accelerated by increasing the alkalinity of the medium, and is of first order with respect to the aldehyde at low aldehyde concentrations. The rate, however, increases above that required for first-order dependence both at high aldehyde and at high alkali concentrations, and examination of products showed that aldolisation products were being formed concurrently.

It is not proposed to examine this oxidation in further detail since the present work is sufficient to confirm the view that the 1-electron oxidation of aliphatic aldehydes regularly occurs *via* the enol so as to give a resonance-stabilised radical and therefrom a product oxidised in the α-position to the CHO group.

EXPERIMENTAL

Potassium nitrosyl disulphonate was prepared as described by Palmer,[5] at <0° during the whole procedure, washed free from sulphite with 10% aqueous potassium hydroxide, then with anhydrous ethanol, and stored in a vacuum. Solid which had been kept for more than 3 days was discarded, and fresh aqueous solutions were prepared each day. Freshly prepared solid, when analysed by means of iodine–thiosulphate, had a purity of at least 99·7%. 0·05M-Solutions in carbonate–bicarbonate buffers changed very little in colour intensity during 50 hr. at room temperature. The colorimetric measurements were made with a "Spekker" photoelectric absorptiometer and light of about 550 mμ (yellow-green, no. 605, filters). Linear plots relating absorption to concentration were regularly obtained so that at the molarities used the dissociation of the orange dimeric salt to the purple $\cdot O\cdot N(SO_3K)_2$ free radical must be complete. To adjust changes in its sensitivity the absorptiometer was calibrated daily.

Before use the aldehydes were freshly distilled from iron wire in a current of nitrogen, and solutions were made up by weight in distilled water which had been flushed with nitrogen. Buffer solutions were prepared from "AnalaR" sodium carbonate and sodium hydrogen carbonate so as to have a constant ionic strength corresponding to that of 0·4M-sodium carbonate. pH Measurements were made with a Doran instrument and an "Alkacid" glass electrode.

For kinetic measurements solid Frémy's salt was dissolved in the requisite buffer solutions, flushed with nitrogen, brought to the requisite temperature, and then mixed in the thermostat with due proportions of the air-free aldehyde solution. A small quantity of each mixture was transferred to a bubbler, and pure nitrogen was slowly passed through this and then through the main bulk of the reactants so that loss of aldehyde as vapour from the reacting mixture was prevented. At intervals samples of the reaction mixtures were pipetted into the optical cells which already contained a known volume of concentrated sodium hydrogen carbonate solution, sufficient to reduce the alkalinity to such an extent that further reaction ceased.

*Investigation of Reaction Products from iso*Butyraldehyde.—(*a*) The colourless oxidised solutions were shown to contain free potassium hydroxylaminedisulphonate, $HO\cdot N(SO_3K)_2$, since treatment with lead dioxide re-formed the purple radical.[3] (*b*) The colourless solution did not give an iodoform reaction until it had been boiled with 30% aqueous sodium hydroxide for

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[5] Palmer, "Experimental Inorganic Chemistry," Cambridge Univ. Press, 1954.

30 min. This is regarded by Conant and Aston [4] as diagnostic for the presence of α-hydroxy*iso*butyraldehyde. (*c*) Warming an oxidised solution with 2 : 4-dinitrophenylhydrazine in hydrochloric acid gave a mixture of orange dinitrophenylhydrazones. These were collected, dissolved in carbon tetrachloride, and passed through acid-washed alumina. By crystallisation, from ethanol, of the poorly separated fractions there were obtained the dinitrophenylhydrazones of *iso*butyraldehyde, m. p. 182°, acetone, m. p. and mixed m. p. 126°, and α-methylacraldehyde, m. p. 204° (Found : C, 48·1; H, 4·0; N, 22·4. Calc. for $C_{10}H_{10}O_4N_4$: C, 48·0; H, 4·0; N, 22·4%).

The measurements shown in the Figure were carried out at pH 9·63 with a buffer containing 16·8 g. of sodium hydrogen carbonate and 39·75 g. of sodium carbonate per l. Both reaction mixtures contained the same initial quantity of aldehyde, but to mixture B there were also added (per l.) 60 g. of sodium perchlorate monohydrate.

THE DYSON PERRINS LABORATORY, OXFORD.

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