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ESR Studies of the Sulfite Radical Anion

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Rapid-mixing flow techniques coupled with ESR measurements have so far enabled us to identify several unstable radicals formed during chemical reactions.[1-4] Further work has now been carried out on the oxidation of bisulfite ions in connection with the biologically significant reaction involving sulfite - bisulfite ions.[5] As a result, we found that the sulfite radical anion, SO_3^-, is formed during the reaction of sodium bisulfite with Ce^{4+}. Since the ESR of the sulfite radical anion in aqueous solutions has not yet been reported, we wish briefly to communicate the ESR of the radical anion and its chemical characteristics.

Experimental

The ESR measurements were carried out on a JEOL-P-10 spectrometer (X-band) with 100 kHz field modulation, in conjunction with a JEOL mixer. This apparatus enabled us to detect radicals formed in the reaction time of the order of 5—100 msec. The spectra were recorded at room temperature. The *g*-values were determined relative to DPPH, for which $g=2.0036$. The concentrations of the spins were approximated to the peak-to-peak height of a given signal. Commercial samples of $Ce(NO_3)_4 \cdot 2\ NH_4NO_3$ and $NaHSO_3$ were used without further purification. Each aqueous solution was acidified by sulfuric acid at pH=1. The concentration was 0.01 M for the cerium salt and 0.1 M for the bisulfite in most experiments. Details of the experimental procedure were previously described.[2]

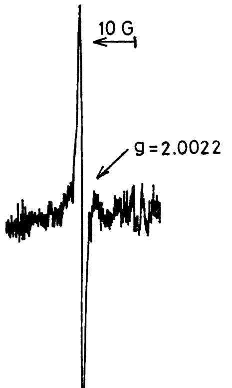

Fig. 1. ESR spectrum of the radical species (SO_3^-) formed during the reaction of Ce^{4+} with $NaHSO_3$ in aqueous solutions.

Results and Discussion

An ESR spectrum characterized by a single line with a nearly isotropic *g*-value was observed, as is shown in Fig. 1, when two solutions, containing Ce^{4+} and HSO_3^- respectively, were subjected to a rapid-mixing flow passing through the ESR cavity. The spectrum was well detectable for reaction times from several to about 100 msec without changing the *g* value (2.0022) and the linewidth of about 2.4 gauss. In view of the strong one-electron oxidizing capability of Ce^{4+}, the sulfite radical anion, SO_3^-, must be formed according to the reaction:

$$HSO_3^- + Ce^{4+} \longrightarrow SO_3^- + H^+ + Ce^{3+} \qquad (1)$$

While no ESR has been reported hitherto with respect to the SO_3^- ion in aqueous solutions, its formation has already been reported for γ-irradiated K_2SO_4 crystals,[6] where an axially symmetric resonance line at the *g*-value of 2.0023—2.0033 has been attributed to the SO_3^- radical anion. The irradiated K_2SO_4 sample gave rise to another spectrum charaterized by a highly anisotropic *g*-tensor (2.0486, 2.0082, 2.0037), which was attributed to the SO_4^- radical anion. The average *g*-value of the SO_4^- is calculated therefrom to be 2.0235, which is much greater than the value observed above. Thus, the spectrum of Fig. 1 can probably be assigned to SO_3^-. This supposition was confirmed by the following observation.

It is well known that pyrosulfite is hydrolyzed according to the reaction:

$$S_2O_5^{2-} + H_2O \longrightarrow 2HSO_3^- \qquad (2)$$

The mixture of Ce^{4+} and pyrosulfite may, then, be expected to produce the SO_3^- radical anion. Experiments have in fact shown that the same signal as that of Fig. 1 was obtained when pyrosulfate and Ce^{4+} were subjected to rapid-mixing flow reactions.

Apart from the ESR measurements, the sulfate radical anion, SO_4^-, is a well established intermediate in the thermal and photochemical decomposition of inorganic persulfates. The one-electron reduction of persulfate ions by Fe^{2+} or Ti^{3+} is known also to produce the radical anion according to:

$$S_2O_8^{2-} + Fe^{2+} \longrightarrow SO_4^{2-} + SO_4^- + Fe^{3+} \qquad (3)$$

Unfortunately, no ESR signal ascribable to the SO_4^- radical anion has been reported in aqueous solutions. However, in the presence of olefinic compounds, the rapid-mixing flow technique has provided ESR evidence for the formation of SO_4^- adducts,[7] suggesting that the

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2) T. Ozawa, Y. Kirino, M. Setaka, and T. Kwan, *Nippon Kagaku Zasshi*, **92**, 304 (1971).

3) Y. Kirino and T. Kwan, *Chem. Pharm. Bull.* (Tokyo), **19**, 718 (1971).

4) Y. Kirino and T. Kwan, *ibid.*, **19**, 831 (1971).

5) H. Hayatsu, *J. Amer. Chem. Soc.*, **91**, 5693 (1969).

6) V. V. Gromov and J. R. Morton, *Can. J. Chem.*, **44**, 527 (1966).

7) R. O. C. Norman, P. M. Storey, and P. R. West, *J. Chem. Soc.*, *B*, **1970**, 1087.

SO_4^- radical anion was present, but was very short-lived.

The presence of the SO_2^- radical anion in aqueous solutions of sodium dithionite has also been reported;[8,9] the radical is formed by the monomerization of the dithionite ion:

$$S_2O_4^{2-} \longrightarrow 2SO_2^- \tag{4}$$

We have found an isotropic ESR line for the aqueous solution of sodium dithionite at the *g*-value of 2.0055; this is in accordance with a recent report.[10] A typical ESR spectrum of SO_2^- is shown in Fig. 2. The signal was fairly stable; it remained for reaction times exceeding one hour at room temperature.

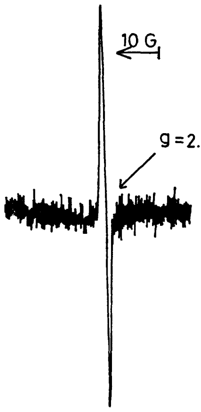

Fig. 2. ESR spectrum of the radical species (SO_2^-) formed in an aqueous solution containing $Na_2S_2O_4$.

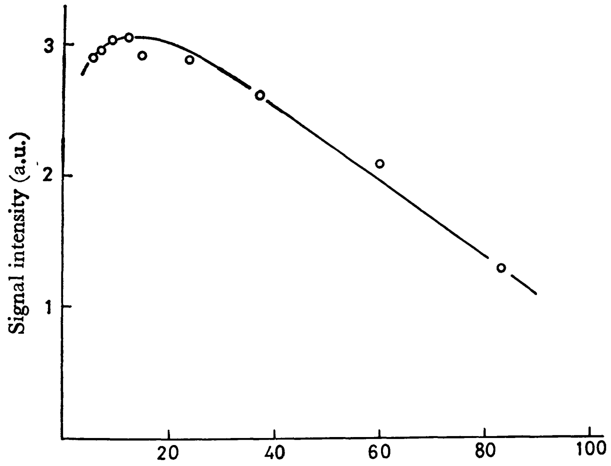

Fig. 3. The signal intensity of SO_3^- *vs.* reaction time relationship.

Figure 3 shows the spin concentrations of SO_3^- against the reaction times. As is shown in Fig. 3, the concentration of SO_3^- reached a maximum at about 10 msec after mixing and gradually decreased thereafter. It was detectable for 100 msec. The stability of the radical anion was, then, distinguishable from that of SO_2^- or SO_4^-. The difference in the thermal stability for SO_3^- and SO_4^- has been noted also in γ-irradiated K_2SO_4 crystals;[6] accordingly, the SO_4^- radical was much less stable than the SO_3^-, which is consistent with the present observation in aqueous solutions. Consequently, the possibility that the spectrum of Fig. 1 could be due to either SO_2^- or SO_4^- can be excluded on the basis of the argument of their stability.

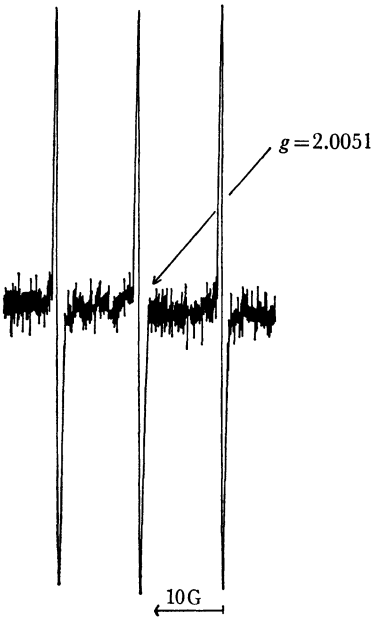

Fig. 4. ESR spectrum of the radical species ($ON(SO_3^-)_2$).

To compare the chemical reactivity of SO_3^- with that of SO_4^-,[7] we further investigated the reaction of SO_3^- with inorganic and organic additives by utilizing the rapid-mixing technique. Some results will be mentioned below. The SO_3^- signal appeared and was stable enough when an ethanol-containing bisulfite was mixed with the Ce^{4+} solution, while the signal was absent when allyl alcohol was substituted for ethanol. These results suggest that the SO_3^- reacts only with olefinic compounds, perhaps forming SO_3^- adducts.

A triplet signal was obtained (Fig. 4) when a $NaNO_2$-containing bisulfite was allowed to react with Ce^{4+}. The signal was exactly the same as that obtainable from potassium nitrosodisulfonate, the Fremy salt ($\cdot O\text{-}N(SO_3K)_2$). This radical may be formed by the one-electron oxidation of the hydroxylamine sulfonate ion, $HON(SO_3^-)_2$, by Ce^{4+} (6). The latter can be formed by the reaction of NO_2^- with HSO_3^- according to (5):[11]

$$NO_2^- + 2HSO_3^- \longrightarrow HON(SO_3^-)_2 + OH^- \tag{5}$$

$$HON(SO_3^-)_2 + Ce^{4+} \longrightarrow ON(SO_3^-)_2 + H^+ + Ce^{3+} \tag{6}$$

The above findings suggest that the SO_3^- radical anion is less reactive than the SO_4^-, the reactivity of which has already been worked out by Norman *et al.*[7] The problem of the relative reactivity of the SO_2^-, SO_3^-, and SO_4^- radical anions awaits further investigations.

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[9] S. Lynn, R. G. Rinker, and W. H. Corcoran, *J. Phys. Chem.*, **68**, 2363 (1964).

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