JOURNAL OF CATALYSIS 15, 209–213 (1969)

NOTES

The ESR Evidence of VO^{3+}–Hydroperoxy Complex Radical

The ESR spectra of radicals formed on mixing titanium(III) salts and hydrogen peroxide have been discussed by many workers (*1–5*). None of them, however, showed hyperfine (hf) splitting caused by the metal ion, hence throwing doubt whether the radical species are *free* or *complexed*. Recently, Fischer, also investigating this system, obtained an ESR spectrum accompanied by some "satellite" lines (*6*). Unfortunately, the "satellite" signals were too small to distinguish from noise, although the worker claimed titanium hyperfine structure from the spectrum. In the present note, an ESR evidence for complexed radical species is presented for the vanadium(IV) oxysulfate, $VOSO_4$, and hydrogen peroxide in acidified aqueous solutions.

The detection of radicals formed upon mixing $VOSO_4$ (0.01 *M*) and H_2O_2 (0.5 *M*) both in sulfuric acid (pH 2) was carried out by rapid-mixing flow techniques coupled with ESR. A JEOL-P-10 type (*X*-band) spectrometer with 100 kcps field modulation and a JEOL-mixer were used for this purpose. Reaction times of the order of 5–100 msec were calculated, as usual, from the observed flow rate and the known holdup volume. For reaction times less than 30 msec, ESR spectra consisting of eight resonance lines were observed, and this signal, also appearing in the absence of H_2O_2, was assigned to VO^{2+} in the light of the reported materials (*7*).

The VO^{2+} signal decayed however at lower flow rates, and for reaction times greater than 30 msec another new signal developed overlapping with one of the eight lines due to VO^{2+}. The new signal was characterized again with eight lines but with much less hf coupling constant, suggesting that the radical species interact with the vanadium nucleus (^{51}V, 99.75%, $I = 7/2$). Its ESR parameters were found to be

$$g = 2.0116 \qquad A = 4.5\ \mathrm{G} \qquad \Delta H = 1.0\ \mathrm{G}$$

In Fig. 1 is shown a typical spectrum for this radical. The radical was fairly stable; its lifetime was estimated as about 10 sec.

Recently, Kasansky *et al.* (*8*) obtained an anisotropic hf splitting in eight lines for adsorbed O_2^- on supported vanadium pentoxide, suggesting that adsorption centers are the surface vanadium ions. The average *g* value and hf coupling constant

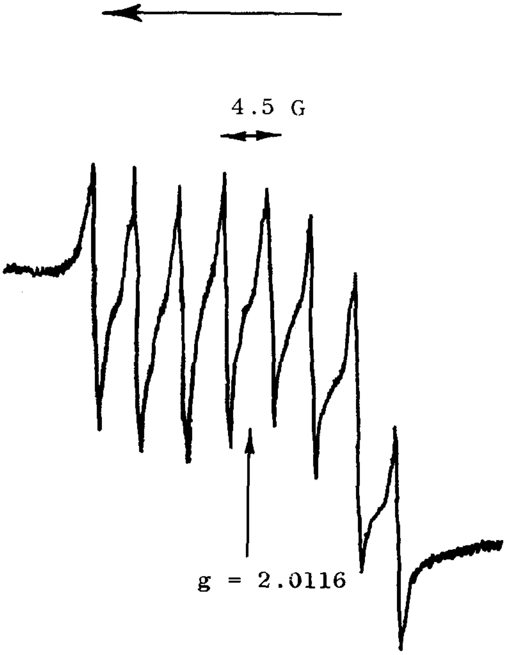

FIG. 1. ESR spectrum of the $VOSO_4$–H_2O_2 system at 25°C.

were calculated, according to their spectra, as

$$g_{\mathrm{av}} = 2.0136 \qquad A_{\mathrm{av}} = 8.9\ \mathrm{G}$$

The "average" g and A values are the isotropic ones computed from the three g-values ($g_1 = 2.025$, $g_2 = 2.011$, $g_3 = 2.005$) and from the three hf coupling constants ($A_1 = 13.2 \times 10^{-4}\mathrm{cm}^{-1}$, $A_2 = 6.4 \times 10^{-4}\mathrm{cm}^{-1}$, $A_3 = 5.6 \times 10^{-4}\mathrm{cm}^{-1}$) reported in Ref. (*8*) according to the formulas:

$$\begin{aligned} g_{\mathrm{av}} &= \tfrac{1}{3}(g_1 + g_2 + g_3) = 2.0136, \\ A_{\mathrm{av}} &= \tfrac{1}{3}(A_1 + A_2 + A_3) \\ &= 8.4 \times 10^{-4}\mathrm{cm}^{-1} = 8.9\ \mathrm{G}. \end{aligned}$$

These values are somewhat different from those obtained for the $VOSO_4$–H_2O_2 system.

The radical species of Fig. 1 may probably be ascribable to the HO_2 radical rather than the OH radical because the g value (2.0116) is much less than those (2.0267–2.0388) reported by Gunter (*9*) for the OH radical generated in various hydrate crystals. The HO_2 radical is expected to ionize depending on pH as

$$HO_2 \rightleftarrows O_2^- + H^+$$

Since the pK of HO_2 has been estimated as 4.4 ± 0.4 (*10*), the ionized form or O_2^- should be excluded under the present pH, unless complexing affects the pK of HO_2 to a great extent.

Consequently, we can consider that the VO^{3+}–HO_2 complex radicals are formed upon mixing vanadium(IV) oxysulfate and hydrogen peroxide. The VO^{3+}–HO_2 complex would have been produced via $VO^{2+} + H_2O_2 \rightarrow VO^{3+} + OH + OH^-$, $OH + H_2O_2 \rightarrow H_2O + HO_2$, $VO^{3+} + HO_2 \rightarrow VO^{3+}$–$HO_2$. The complex was rather stable and may not be regarded as active intermediates in the reactions with organic additives. Kinetic evidence of this sort will be reported elsewhere.

References

1. Dixon, W. T., and Norman, R. O. C., *Nature* **196,** 891 (1962).

2. Piette, L. H., *Am. Chem. Soc. Meeting,* April, 1964.

3. Sicilio, F., Florin, R. E., and Wall, L. A., *J. Phys. Chem.* **70,** 47 (1966).

4. Chiang, Y. S., Craddock, J., Mickewich, D., and Turkevich, J., *J. Phys. Chem.* **70,** 3509 (1966).

5. Florin, R. E., Sicilio, F., and Wall, L. A., *J. Phys. Chem.* **72,** 3154 (1968).

6. Fischer, H., *Ber. Bunsen.* **71,** 687 (1967).

7. Pake, G. E., "Paramagnetic Resonance," p. 111. Benjamin, New York, 1962.

8. Shvets, V. A., Saricher, M. E., and Kasansky, V. B., *J. Catalysis* **11,** 378 (1968).

9. Gunter, T. E., *J. Chem. Phys.* **46,** 3818 (1967).

10. Czapski, G., and Bielski, B. H. J., *J. Phys. Chem.* **67,** 2180 (1963).

M. Setaka
Y. Kirino
T. Ozawa
T. Kwan

Faculty of Pharmaceutical Sciences,
The University of Tokyo,
Bunkyo-ku, Tokyo, Japan

Received March 11, 1969;
revised April 23, 1969

Some Acid Properties of H_2PtCl_6

In studying the relation between the catalytic properties of Pt–Al_2O_3 and the reaction of Al_2O_3 with the H_2PtCl_6 impregnation solution, we found it necessary to answer two questions concerning aqueous H_2PtCl_6: (i) How can the acid content of a solution of H_2PtCl_6 be determined, since at least one side reaction occurs when a strong base is used to titrate? (ii) How strong an acid is H_2PtCl_6? One might expect H_2PtCl_6 to be a strong acid, but there seems to be no evidence in the literature that this question has actually been answered. Because of the extensive use