0.4–3.0 *M*, radioactive assays after 6 days showing low solubilities of about 3 mg. Am/liter. However, the rate of precipitation after initial oxidation was dependent upon carbonate concentration. For example, 4.5 hours after oxidation in 0.4 *M* potassium carbonate solution, the americium concentration remaining in solution was ~60 mg./liter, while in 3.0 *M* potassium carbonate the unprecipitated americium was ~23 mg./liter.

It was found possible to dissolve quickly the insoluble americium compound in 0.1 *M* sulfuric acid after washing with distilled water. The solution appeared colorless and while being measured in the spectrophotometer, the absorption at 5030 Å. was checked at intervals as an index of the Am(III) present. During the course of the measurement (2.5 hours), the Am(III) increased from an initial concentration of 2% to a final value of 5%. By correcting the light absorption due to Am(III), the curve shown in Fig. 1c was obtained which is taken to be characteristic of Am(V) in 0.1 *M* sulfuric acid solution. The absorption bands are at 5150 and 7200 Å. with molar extinction coefficient 48 and 66, respectively.

Final proof of the oxidation state of the new form was obtained by titration with a reducing agent. In a typical experiment, americium was oxidized and precipitated as described, washed six times with distilled water, and dissolved in 0.1 *M* sulfuric acid. It was precipitated again by addition of potassium carbonate, washed four times again with water and dissolved in 0.1 *M* sulfuric acid. From this solution an aliquot of 0.100 ml. was removed and the concentration measured[10] as 7.24 ± 0.03 millimolar. Measurement of the absorption spectrum showed 4% of the americium to be Am(III).

Exactly 0.030 ml. of 0.0502 *N* ferrous ion solution was added, and as well as could be told by spectral analysis, reduction to Am(III) was complete. The solution was transferred quantitatively to a micro titration dish and the excess ferrous ion titrated with standard ceric solution using ferrous phenanthroline as an indicator. It was found that 1.367 microequivalents of ferrous ion had been oxidized by the americium which upon calculation showed the oxidized state to have 1.96 equivalents/mole.

Since the forms of Pu(V) and Np(V) ions in acid solution have been shown[11] to be PuO_2^+ and NpO_2^+, respectively, we may expect Am(V) to be AmO_2^+ under similar conditions. No attempt has been made to identify the Am(V) compound which precipitates from carbonate solution.

This work was performed under the auspices of the U. S. AEC.

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[10] Measured by α-particle assay using a half-life of 475 years.

[11] K. A. Kraus and G. E. Moore, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 4.19 (McGraw-Hill Book Co., Inc., New York, N. Y., 1949); L. B. Magnusson, J. C. Hindman and T. J. La-Chapelle, *ibid.*, Paper No. 15.4.

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Oxygen Atom Transfer during the Oxidation of Aqueous Sodium Sulfite

BY E. R. S. WINTER AND H. V. A. BRISCOE

The very interesting communication of Halperin and Taube[1] on the above subject prompts us to put on record some experiments upon similar lines which were performed in 1939.[2] In this work we studied briefly the oxidation by normal oxygen gas and by normal hydrogen peroxide of normal sodium sulfite, dissolved in water containing O^{18} in excess of the normal abundance. In both cases the oxygen atom which was transferred to the sulfite ion came from the oxidizing agent, and not from the water.

The experiments upon oxygen oxidation were performed by dissolving 1.5 g. of Analar hydrated sodium sulfite ($Na_2SO_3 \cdot 7H_2O$) in 3 ml. of enriched water at room temperature (≈ 18°). This solution was exposed to oxygen, confined in a gas buret, until no further absorption of gas took place: in all cases the absorption was close to the theoretical requirements. That oxidation was complete was checked by titration with $KMnO_4$ and also by gravimetric estimation of the sulfate formed. The O^{18} content of the water was measured before and after the oxidation by determination of the water density, after vigorous purification, by the semi-micro silica float method.[3] The results are summarized in Table I: it is clear from experiments 4 and 5, where the solution was left for some 72 hours at room temperature—a time longer than required for the completion of oxidation in experiments 1, 2, 3 and 6—that the exchange of the sulfite ion is negligible under these conditions, the observed decrease in water density in p.p.m., $\Delta\gamma d$, being essentially that to be expected from dilution with the water of crystallization of the sodium sulfite. Experiments 1, 2, 3 and 6, show conclusively that the over-all reaction $2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$ proceeds without exchange of oxygen with the solvent water.

TABLE I

Expt.	Vol. of O_2 adsorbed, ml. N. T. P. Obs.	Vol. of O_2 adsorbed, ml. N. T. P. Calcd.	$\Delta\gamma d$ obs.	$\Delta\gamma d$ calcd. for $7H_2O$ from sulfite	Experimental conditions
1	66.0	66.6	−79	−78	Oxygen
2	66.2	66.6	−81	−78	from
3	66.8	66.6	−80	−78	cylinder
4	..	..	−80	−78	In atmosphere of nitrogen
5	..	..	−79	−78	*In vacuo*
6	66.5	66.6	−80	−78	In oxygen, trace $CuSO_4$ added

$\Delta\gamma d$ calcd. for $7H_2O + 0 = -91.$
$\Delta\gamma d$ calcd. for $7H_2O + 3.0 = -117.$
$\Delta\gamma d$ calcd. for $7H_2O + 4.0 = -130.$

Examination of the various chain mechanisms which have been proposed for this reaction—involving, *e.g.*, either the radical HSO_5[4] or the radical ion SO_5'[5] shows that on either hypothesis the above result might be expected, since oxygen transfer involving oxygen from the water molecules, would not be expected to occur. It is however unfortunate that our experiments were of necessity (because of the relatively small enrichments of H_2O^{18} available at the time) performed using solutions very much more concentrated than those which have been used in investigations of the chain reaction. It would be very interesting to know if these results are confirmed in more dilute solutions.

For experiments upon the oxidation of sodium sulfite with hydrogen peroxide, the exchange of hydrogen peroxide with water was first examined. Merck perhydrol (aqueous hydrogen peroxide containing 29% H_2O_2 by analysis) was used as a source of hydrogen peroxide. It proved impossible

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[1] Halperin and Taube, THIS JOURNAL, **72**, 3319 (1950).

[2] Winter, Ph.D. Thesis, London University, 1942.

[3] Briscoe, *et al.*, *J. Chem. Soc.*, **1207**, **1948** (1934); Spoor, Ph.D. Thesis, London, 1935.

[4] Franck and Haber, *Sitzungsber. Preuss. Akad.*, 50 (1931).

[5] Backstrom, *Z. physik. Chem.*, **25B**, 122 (1934).

to mix the perhydrol with the heavy water and subsequently separate by physical methods the bulk of the hydrogen peroxide from the water, so that a direct check of the extent of any exchange was not feasible. Instead, 1-ml. lots of the perhydrol were mixed at room temperature with 2-ml. portions of heavy oxygen water, and the solution left for 48 hours with addition of a trace of a catalyst active in promoting the decomposition of hydrogen peroxide. At the end of this time the liquid was raised just to the boiling point to complete the decomposition, and the residual water purified and its density determined. The complete disappearance of the peroxide was confirmed by chemical tests. In a further experiment the mixture of peroxide and heavy water was left for 24 hours at room temperature before addition of the catalyst. The results are shown in Table II, from which it is evident that the decrease in density observed is wholly accounted for by the water produced in the decomposition of the peroxide and that added with the perhydrol, and we conclude that the oxygen evolved did not suffer exchange with the enriched water. Clearly under these conditions there is little if any exchange of the hydrogen peroxide molecule with water: neither does the heterogeneous catalytic decomposition require the active participation of the water molecule.

TABLE II

Catalyst	Obs.	$\Delta\gamma d$ calcd. for 1.0 from H_2O_2	$\Delta\gamma d$ calcd. for 2.0 from H_2O_2
$MnO_2 + Mn_2O_3$	−51	−50	−56
Fe_2O_3	−51	−50	−56
Palladized asbestos	−52	−50	−56
Platinized asbestos	−52	−50	−56
Platinized asbestos added after 24 hr.	−52	−50	−56

The perhydrol was then used to oxidize sodium sulfite: 2 ml. of perhydrol was mixed with 4 ml. of enriched water, and 1.71 g. of finely powdered anhydrous sodium sulfite added slowly with stirring. The temperature of the mixture reached 40° during the oxidation. At the end of the oxidation the mixture was boiled, cooled and the density of the water determined as before. A parallel experiment showed that substances capable of decolorizing permanganate were equivalent to less than 1 ml. of 0.1 *N* $KMnO_4$ at the end of the reaction. With the quantities used above, the decrease in density to be expected due to the water added as perhydrol, including that which would remain after the reaction $H_2O_2 + Na_2SO_3 \rightarrow H_2O + Na_2SO_4$ was $\Delta\gamma d = -50$.

The total decrease to be expected if the second oxygen atom in the hydrogen peroxide molecule suffered exchange with the heavy water was $\Delta\gamma d = -56$, while the total decrease to be expected if the three oxygen atoms of the sodium sulfite also exchanged was $\Delta\gamma d = -65$: the observed decrease in water density was $\Delta\gamma d = -52$, demonstrating that, allowing for the normal error, the experimental technique, and by comparison with the results in Table II, direct transfer occurs of the oxygen atom from the hydrogen peroxide molecule to the sodium sulfite. The experimental error in the water density determinations recorded here is ±1 γd ($1\gamma d$ = 1 in 10^6 of density).

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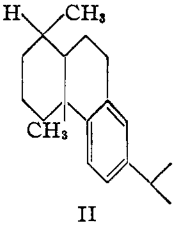
Diphenyl-*t*-dehydroabietinol and its Oxidation Product

BY HAROLD H. ZEISS

In the course of continued work with the resin acids it has become apparent to us that our earlier reported studies in this field are subject to correction. It has been found that the procedure described for the isolation of diphenyl-*t*-dehydroabietinol (I)[1] leads instead to a cleavage product, which, on treatment with hot chromic acid, is oxidized to ketonic material of different structure than that previously proposed.[2] In view of the recently published paper of Brossi, Gutman and Jeger[3] in which the same conclusions are reached, it is considered appropriate to report our results at this time.

Authentic I is obtained from the Grignard reaction between methyl dehydroabietate and phenylmagnesium bromide according to the original procedure, with the exception of subjecting the crude product to crystallization from glacial acetic acid instead of to distillation. The ultraviolet spectrum of the crystalline carbinol, m.p. 139°, is consistent with that of the dehydroabietic-type structure as exemplified by the spectrum of dehydroabietic acid (Fig. 1). If, however, the crude carbinol is vacuum distilled in a Claisen flask, a yellow oil is collected which analyzes correctly for I but which gives an ultraviolet spectrum similar to that of benzophenone. The explanation for this has been secured from the observation that crystalline I, when heated between 190–230° and then cooled to room temperature, is transformed into a yellow liquid which also gives a benzophenone-type spectrum (Fig. 2). The presence of benzophenone is confirmed by its isolation from the mixture.

The thermal cleavage of I is reminiscent of the type experienced by other workers with tertiary alcohols.[4] In this instance the expected products are benzophenone and nordehydroabietane (II. 12-methyl-1,2,3,4,9,10,11,12-octahydroretene).



II

Evaporative distillation and chromatography were

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(1) H. H. Zeiss, THIS JOURNAL, **69**, 302 (1947).

(2) H. H. Zeiss, *ibid.*, **70**, 858 (1948).

(3) A. Brossi, H. Gutmann and O. Jeger, *Helv. Chim. Acta*, **33**, 1730 (1950).

(4) P. Ramart-Lucas, *Ann. chim.*, [8] **30**, 349 (1913); V. Grignard and F. Chambret, *Compt. rend.*, **182**, 299 (1926).