$\Delta F°$ (25° above τ) when $\Delta C_p°$ for the reaction oxygen-acceptor + $^1/_2$ O_2 = oxygen-donor is zero. When $\Delta C_p° \neq 0$, $\Delta H°$ and $\Delta S°$ nevertheless increase, or decrease, together, their increments tending to balance each other off in the second step above, which remains often a useful approximation.

From Fig. 6 one sees that whereas lead nitrate decomposes around 300–400° (level 10 to 4, forming PbO + NO_2 + O_2), there do not appear to be acceptor levels below the highest KNO_3 donor level in KCl doped only with KNO_3, at least at temperatures below the melting point of KCl. The instability of NO_3^- produced during the thermal decomposition of nitrocellulose probably arises from the presence in these instances of the low-lying hydrocarbon level 11. At 150° it is as good an acceptor as H_2.

It should be mentioned, however, that at relatively high temperatures (200–365°) a KI pellet doped with a little KNO_3 produced a number of new bands after several days (Fig. 5). From the growth and decay of these bands with time at several temperatures, it appears that the 2400 and 1750 bands probably belong to the same molecule, or ion, 1685 and 950 to another, and 2150 and 1250 to still others.

Spectrum of CO_2 at High Pressures.—Carbon dioxide appears to be formed *in situ* during the thermal decomposition of nitrate esters in KBr (Fig. 4). The dashed curve in Fig. 7 is a close-up of the 2350 cm.$^{-1}$ band produced in KBr in 55 minutes by the thermal decomposition of nitrocellulose at 157°. To reduce scattering, the pellet had been recompressed to 12,500 p.s.i. For comparison, the spectrum of atmospheric CO_2 is shown, drawn to the same total integrated intensity ($\int \log (I_0/I)$). Recompression to 125,000 p.s.i. (solid curve) continued to diminish the relative intensity of the high frequency branch; the integrated intensity, however, was not noticeably affected. Cooling to liquid nitrogen temperatures further sharpened the band, again with little change in the total integrated intensity. These effects are reversible—warming tends to restore the normal band contour—, reproducible, in KBr and KCl, and relatively permanent at room temperature,

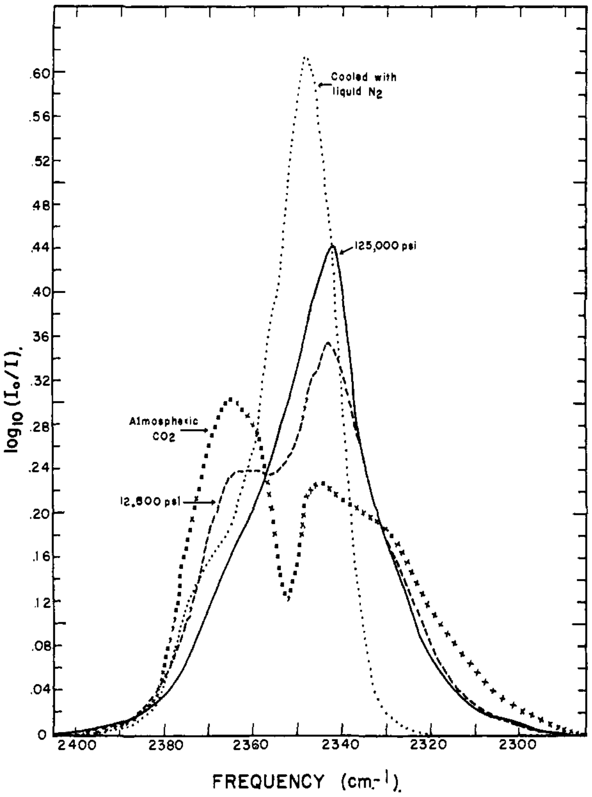

Fig. 7.—Spectra of CO_2 at high pressures.

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MINNEAPOLIS 14, MINN.

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES, BROWN UNIVERSITY]

The Exchange Behavior of Monosubstituted Peroxides

BY GERRIT LEVEY,[1] DONALD R. CAMPBELL,[2] JOHN O. EDWARDS AND JANE MACLACHLAN

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A study of possible isotope exchange between four monosubstituted peroxides and the corresponding anions has been carried out. In three cases (sulfate, benzoate and acetate), no exchange was observed even at the temperature of rapid peroxide decomposition. In the phosphate case, no way of separation of peroxide from anion was found. Mechanistic conclusions are pointed out.

The exchange behaviors of hydrogen peroxide and peroxydisulfate ion have been studied extensively. Hydrogen peroxide does not appear to exchange with either labeled H_2O or OH^- under a variety of conditions.[3] The exchange of radiosulfate ion with peroxydisulfate ion also proceeds very slowly if at all.[4]

In view of the more reactive nature of the unsymmetrical peroxides such as Caro's acid, it was felt worthwhile to find out whether exchange could be detected with them. Results with Caro's acid

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(1) Visiting Summer Research Associate, 1956.

(2) National Science Foundation Predoctoral Fellow, 1956–1957.

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(peroxymonosulfuric acid), peroxybenzoic acid and peroxyacetic acid are presented below. No way to separate peroxymonophosphate from phosphate was found.

Experimental

Materials.—The sulfate and phosphate labeled with S^{35} and P^{32}, respectively, were obtained from Oak Ridge. The C^{14}-labeled acetate and benzoate were obtained from New England Nuclear Corp. Peroxyacetic acid and hydrogen peroxide were gifts of the BECCO Division of Food Machinery and Chemical Corp. Peroxymonophosphoric acid was prepared by the method of Toennies.[5] Peroxymonosulfuric acid was prepared by the method of D'Ans and Friedrich.[6] Peroxybenzoic acid was prepared by the method of Braun[7] using the modifications of Kolthoff.[8] Other standard chemicals, if not reagent grade, were purified before use.

Separation Procedures.—As one of the decomposition products of a peroxyanion is the corresponding oxyanion, the radioactive isotope was employed in the oxyanion in each case. Any activity above experimental error in the peroxide fraction would therefore be attributable to exchange. In order to minimize decomposition, ethylenediaminetetraacetic acid was added to the reaction mixture in the manner carried out by Ball.[9]

Sulfate ion was separated from Caro's acid by precipitation of barium sulfate. The peroxysulfate was then reduced with iodide and the resulting sulfate precipitated as the barium salt. The precipitates were centrifuged (in turn) directly onto counting disks using a centriplater designed and kindly supplied by Ames.[10]

Separation of peroxyacetic acid from acetate ion was achieved by extraction of the aqueous phase with ether. At *p*H 7, the acetate ion is not significantly extracted into the organic phase while peroxyacetic acid largely is. During each experiment, about one-third to one-half of the peroxyacetic acid was decomposed or lost mechanically. The aqueous layer was evaporated down to obtain sodium acetate in which form the samples were counted. The peroxyacetic acid in ether was re-extracted into water and neutralized. The water solution was boiled to effect decomposition of peroxide and evaporated to obtain the residual sodium acetate which was counted. A similar procedure was employed to separate peroxybenzoic acid from benzoate ion.

No satisfactory method for separating peroxymonophosphate from phosphate was found. Analytical tests showed that no peroxide was left after the phosphate had been precipitated by barium hydroxide. Precipitation of phosphate as ammonium phosphomolybdate also caused complete decomposition of the peroxide. It appears that peroxymonophosphates, like peroxymonosulfates,[9] have decomposition processes which are catalyzed by base and by molybdate ion.

Counting Procedures.—The three isotopes are β-emitters, thus all of the samples were counted with a thin-window Geiger tube in a constant geometry shield. Data are recorded in units of counts per minute (c.p.m.) above the background of 16 c.p.m. In all cases given, the samples were of such weight per unit area that they could be considered infinitely thick; thus the c.p.m. values can be directly compared. No coincidence corrections have been made.

Results and Discussion

In Table I, the data of the sulfate–peroxymonosulfuric acid exchange experiments are presented. In all cases, the amount of activity in the peroxide fraction is very small and almost certainly results from imperfect, but quite good, separations of mother liquor from the precipitated barium sulfate.

In Table II, the data of the acetate–peroxyacetic acid and of the benzoate–peroxybenzoic acid experiments are presented. Again the amount of activity found in the peroxide fraction is small. The method of separation is less reliable than in the sulfate case and therefore a greater contamination in the peroxide fraction was expected. The results for experiments C2, C3, C5, C6, C7, C8, C11, C12 and C13 are conclusive in indicating 1% or less exchange under such conditions. In the other experiments, a greater amount of exchange may be indicated by the data, but it is believed to be unlikely that these results are outside the experimental error. In this connection, experiment C9 which was worked up immediately after mixing at room temperature shows about 3% apparent exchange, while other experiments which would be expected to show a greater amount of exchange (*i.e.*, C7 and C8) show considerably less; one can conclude therefore that the limits of experimental error are at least ±3%. As peroxyacetic and peroxybenzoic acids decompose fairly rapidly at the higher temperatures employed, it probably would not be possible to obtain more definitive data; the rate of decomposition seems to be much larger than the rate of exchange.

It is to be noted that a particular *p*H range was chosen in each case. The ranges correspond to those for which the attacking nucleophiles (sulfate, benzoate and acetate) are in their anion forms, whereas the peroxide still retains a proton. It was expected that these ranges would correspond to that of greatest rate of OH^+ transfer, and that hydrolysis and decomposition would be minimized. Also in these *p*H ranges, it is unlikely that the reaction of any impurity hydrogen peroxide with anions would occur thereby causing an apparent exchange.

TABLE I

EXCHANGE RESULTS FOR PEROXYMONOSULFURIC ACID

Expt.	$[SO_4^=]$	$[HSO_5^-]$	*p*H	Temp., °C.	Time	$SO_4^=$, c.p.m.	HSO_5^-, c.p.m.
S-1a	0.12	0.18	~2	~25	3 days	50,000	55[a]
S-1b	.12	.18[b]	~2	100	30 min.	35,000	54
S-2	.09	.13	3.2	~25	4 days	40,000	25[c]
S-3	.22	.17[d]	3.5	[e]	[e]	52,000	276[f]

[a] Average of four different separations (60, 63, 43 and 48 c.p.m.). [b] Decreased to 0.14 *M* during the reaction time. [c] Average of two separations (24 and 25 c.p.m.). [d] Decreased to 0.15 *M* during the reaction time. [e] At room temperature for two days, then at 65° for 10 min. [f] Average of two separations (136 and 416 c.p.m.); from the same initial solution. The quantitative separation of HSO_5^- from $BaSO_4$ resulted in increased possibility of contamination of the HSO_5^- solution by $BaSO_4$. The lower value indicates the cleaner separation, but much of this activity probably also results from imperfect separation.

Like the symmetrical peroxides, the three unsymmetrical peroxides undergo exchange reactions very slowly. It seems appropriate to point out that one can conclude that, as a general rule, attack on peroxides by an oxygen function is an unlikely process. The results presented here bear out the earlier conclusion that peroxides are more

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TABLE II

EXCHANGE RESULTS FOR PEROXYACETIC ACID

Expt.	$[CH_3CO_2OH]$	$[CH_3CO_2^-]$	pH	Temp., °C.	Time, min.	% lost[c]	CH_3CO_2OH, c.p.m.	$CH_3CO_2^-$, c.p.m.	% activity as CH_3CO_2OH
C1	0.09	0.13	6	60	30	n.d.	437	5082	8.6[a]
C2	.15	.15	6	25	6 hr.	40	25	5533	0.4
C3	.15	.15	6	50	30	43	26	5330	0.5
C4	.15	.15	6	75	30	54	89	5270	1.7
C5	.25	.25	6	25	0	0	13	5055	0.3[b]
C6	.25	.25	6	25	0	0	18	5027	0.4[b]
C7	.30	.30	6	75	30	48	53	5102	1.0
C8	.30	.30	6	75	30	45	41	5138	0.8
C9	.20	.20	6	25	0	0	175	5089	3.4[b]

EXCHANGE RESULTS FOR PEROXYBENZOIC ACID

Expt.	$[C_6H_5CO_2OH]$	$[C_6H_5CO_2^-]$	pH	Temp., °C.	Time, min.	% lost[c]	$C_6H_5CO_2OH$, c.p.m.	$C_6H_5CO_2^-$, c.p.m.	% activity as $C_6H_5CO_2OH$
C10	0.030	0.03	7	50	30	n.d.	338	13280	2.5
C11	.039	.04	7	50	30	38	91	13089	0.7
C12	.076	.08	7	50	30	30	133	13099	1.0
C13	.066	.07	7	50	30	34	66	13080	0.5

[a] H_2O_2 present. [b] Sample immediately worked up without heating. [c] n.d. signifies not determined.

susceptible to attack by a polarizable nucleophile than by a basic nucleophile.[11] Thus, free-radical mechanisms for certain peroxide reactions, such as the decomposition of peroxydisulfate ion in water and as alcohol oxidation by this ion, would seem to be more reasonable than postulations of electrophilic attack on oxygen by the peroxide.

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PROVIDENCE, R. I.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

The Heat Capacities and Thermodynamic Properties of Crystalline and Vitreous Anhydrous Sodium Tetraborate from 6 to 350°K.

BY EDGAR F. WESTRUM, JR., AND GEORGE GRENIER

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The heat capacities of crystalline and vitreous anhydrous sodium tetraborate ($Na_2B_4O_7$) have been determined from about 6 to 350°K. by adiabatic calorimetry. Values of the heat capacity and the derived thermodynamic functions have been computed and tabulated. Molal values at 298.15°K. of the heat capacity at constant pressure, entropy, enthalpy increment ($H^\circ_T - H^\circ_0$), and free energy function are: 44.64 cal./deg., 45.30 cal./deg., 7262 cal., and −20.94 cal./deg., respectively, for the crystalline modification. For the vitreous modification, the molal values at 298.15°K. of the heat capacity at constant pressure, entropy increment ($S^\circ_T - S^\circ_0$), and enthalpy increment ($H^\circ_T - H^\circ_0$), are: 44.42 cal./deg., 44.39 cal./deg., and 7127 cal., respectively.

Introduction

Despite the use of borax and related materials in ceramic technology for many centuries and their widespread utilization in current chemical technology, reliable thermodynamic data on alkali borates are relatively rare. Data in the chemical literature on the physical properties of anhydrous vitreous and crystalline sodium tetraborate[1] are concerned primarily with melting point and phase equilibrium studies[2] on the Na_2O–B_2O_3 systems. Although two or possibly three distinct crystallographic phases of this material exist,[2] the material prepared for this work is the α-form and is that ordinarily obtainable and commercially available. No evidence for an enantiotropic inversion between the various forms has been found,[2] despite a careful search from below 500° to the melting point. The rate of conversion of β to α is very slow and the reverse transformation has not been observed.

Experimental

Preparation and Purity of Crystalline Sodium Tetraborate.—The sodium tetraborate sample was prepared by crystallizing a dehydrated sample of analytical reagent grade sodium tetraborate decahydrate from the molten state under carefully controlled conditions.[3] Since rapid cooling or prolonged periods of heating at temperatures appreciably higher than the melting point of 742.5°[2] result in glass formation, it is essential for crystal growth that the temperature does not exceed 760° nor even remain at this value for more than ten minutes, and that a controlled rate of cooling be maintained. These conditions were achieved by heating in an electric muffle furnace. After gradually decreasing the temperature in the muffle from 750 to about 300° over ten hours, the covered platinum dish containing the sample was transferred to a desiccator containing phosphorus pent-

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(1) We use the designation sodium tetraborate to refer to the chemical composition $Na_2B_4O_7$, although a contrary usage is occasionally found (*Cf.* ref. 2).

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