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Infrared Investigation of the Thermal Decomposition of Di-*t*-butyl Peroxide and Nitrate Esters in Potassium Halide Pressed Disks, and the Spectrum of Carbon Dioxide at High Pressures[1]

BY HENRY A. BENT AND BRYCE CRAWFORD, JR.

RECEIVED DECEMBER 7, 1956

Dispersion in potassium halide pellets appears to be a safe and convenient way to study spectroscopically decomposition of unstable compounds. In the infrared, the thermal decomposition of di-*t*-butyl peroxide has been followed in pellets of KBr up to relatively high temperatures, products identified, and the rate constant for scission of the O–O bond found to be $1.45 \times 10^{16}e^{-38.0(\text{kcal.})/RT}$ sec.$^{-1}$. Nitrate esters produce NO_3^- and CO_2 in KCl, KBr and KI. Some temperature dependent oxygen atom free energy levels are developed for the anhydrous nitrate–potassium halide system, and spectra are given of CO_2 under apparently high compression.

During an investigation of the flame decomposition of a nitroglycerine–nitrocellulose double-base propellant by infrared spectroscopy, we obtained a nice spectrum of nitrocellulose dispersed in a potassium bromide matrix, following the pellet technique recently developed by Stimson and O'Donnel for obtaining the spectrum of solids.[2,3]

On heating, new bands appeared in the spectrum of these pellets. It occurred to us that this might, in fact, be a convenient, and safe, way to follow the thermal decomposition of nitrocellulose; as well, perhaps, as other unstable compounds.

The initial step in the decomposition of nitrate esters, most investigators agree, is scission of the $O–NO_2$ bond to give NO_2 and an alkoxyl radical[4–6]

$$RONO_2 \longrightarrow RO\cdot + NO_2 \qquad (1)$$

What happens after this is less certain. The NO_2 complicates matters not just a little.

Simpler, but similar in the initial production of alkoxyl radicals, is the decomposition of organic alkyl peroxides, the first step being scission of the RO–OR bond to give two alkoxyl radicals

$$RO\text{–}OR \longrightarrow 2RO\cdot \qquad (2)$$

followed by radical dismutation, recombination and hydrogen abstraction.[7,8]

We chose to look first at di-*t*-butyl peroxide. Pioneering work on the decomposition of this peroxide has been carried out in several laboratories.[9–11] At room temperature it is a liquid, and fairly stable.

Experimental

Pellet Preparation.—Pellets were manufactured on a Carver hydraulic press (20,000 lb. thrust on a 1.25 in. ram) in a 2 in. × 1.25 in. die, which could be evacuated, equipped with plungers of hardened steel 0.5 in. in diameter. The potassium halides—KCl, KBr and KI—were well ground, oven dried and reground before using. Other inorganic salts, such as potassium nitrate, were dry-mixed with the matrix, sometimes with a little Wig-L-Bug vibrator, but usually by hand. Liquids—such as ethyl nitrate and the di-*t*-butyl peroxide (obtained from Jasonols Chemical Corp., Brooklyn, N. Y.)—were added dropwise from a syringe to the powdered potassium halide resting on the bottom plunger in the die, just prior to pressing. Pellets with liquids dispersed in them—we have tried also acetone, methyl ethyl ketone, chloroform and α-chloronaphthalene—are usually cloudy; this, however, does not seem to bother particularly in the infrared. Our optically best nitrocellulose dispersions were obtained by saturating finely powdered KCl, KBr or KI with a non-aqueous solution of the nitrate ester, followed by slow evaporation of the solvent, careful mixing and regrinding with roughly an equal amount of fresh potassium halide, and compression. Our pellets were 0.5 in. in diameter and 1–15 mm. thick.

Heat Treatment.—In preliminary, and later vacuum-line experiments, pellets were heated under an infrared lamp; in kinetic runs, in a thermostated oven, temperature constant to ±0.25° or better. Invariably pellets become increasingly cloudy on heating and sometimes even on standing at room temperature. We suspect devitrification of the matrix, a process that might be expected to accelerate with rising temperature; and we were not able to stop this in several trials with mixed matrices, like KCl–KBr; indeed, this only seemed to intensify the problem. Consequent scattering and deterioration of optical transparency was often severe above 2000 cm.$^{-1}$.

Recompression.—This technique proved quite useful in cases of severe scattering. Devitrified pellets were simply put back in the die and recompressed. Often one-quarter to one-tenth the initial compression pressure was sufficient to restore optical transparency.

Spectra.—Surveys and kinetic data were run on a Perkin-Elmer Model 21 double-beam spectrometer equipped with sodium chloride optics; that of CO_2 trapped in potassium halide matrices on a model 12C double-pass spectrometer with a lithium fluoride prism. For low temperature liquid nitrogen runs pellets were mounted in a cold cell similar to that described by Wagner and Hornig.[12]

Results and Discussion

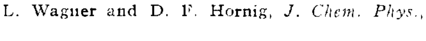
Thermal Decomposition of Di-*t*-butyl Peroxide in KBr.—The radical dismutation

$$(CH_3)_3CO\cdot = (CH_3)_2CO + CH_3\cdot$$

hydrogen abstraction

$$CH_3\cdot \longrightarrow CH_4 \text{ and } (CH_3)_3CO\cdot \longrightarrow (CH_3)_3COH$$

and recombination



$$\cdot CH_2(CH_3)_2CO\cdot \longrightarrow (CH_3)_2C\text{—}CH_2 \text{ (with O bridging C and CH}_2\text{)}$$

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[1] This research was supported by the U. S. Navy, Bureau of Ordnance, through contract with the University of Minnesota.

[2] (a) M. M. Stimson and M. J. O'Donnel, THIS JOURNAL, **74**, 1805 (1952); (b) U. Schiedt and H. Z. Rheinwein, *Naturforsch.*, **76**, 270 (1952).

[3] J. B. Jensen, *Acta Chem. Scand.*, **8**, 393 (1954).

[4] G. K. Adams and C. E. H. Bawn, *Trans. Faraday Soc.*, **45**, 494 (1949).

[5] L. Phillips, *Nature*, **165**, 564 (1950).

[6] J. B. Levy, THIS JOURNAL, **76**, 3254, 3790 (1954).

[7] A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 57–72.

[8] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1954, pp. 232–236.

[9] N. A. Milas and D. M. Surgenor, THIS JOURNAL, **68**, 205, 643 (1946).

[10] P. George and A. D. Walsh, *Trans. Faraday Soc.*, **42**, 94 (1946).

[11] J. H. Raley, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **70**, 88, 1336 (1948).

[12] E. L. Wagner and D. F. Hornig, *J. Chem. Phys.*, **18**, 299 (1950).

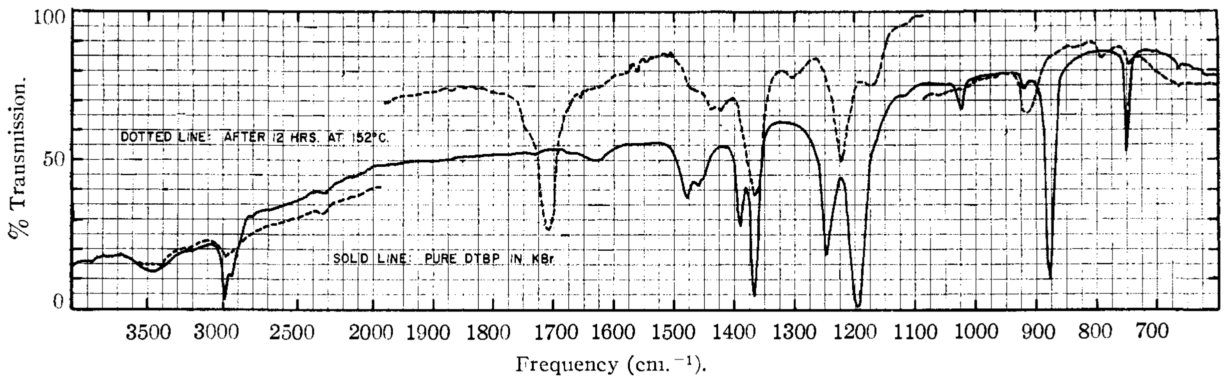

Fig. 1.—Spectra of di-*t*-butyl peroxide and decomposition products in KBr.

mechanism of Vaughan, *et al.*,[11] accounts fairly well for the new bands that appear in the spectra of DTBP dispersions in KBr (Fig. 1).

BANDS APPEARING IN THE THERMAL DECOMPOSITION OF DTBP IN KBR

Band	Assignment
1705 vs	C=O (mainly acetone)
1300 w	Methane
1220 s	Acetone
1170 w	Methyl ethyl ketone (?)
910 m	*t*-Butyl alcohol + something else
785 w	Isobutylene oxide (?)

The gradual disappearance of the O–O stretch at 875 cm.$^{-1}$ (Fig. 1 and Table I) follows first-order kinetics for quite some while at 127° (Fig. 2), and lower temperatures (at 149° the apparent first-order constant steadily decreased with time).

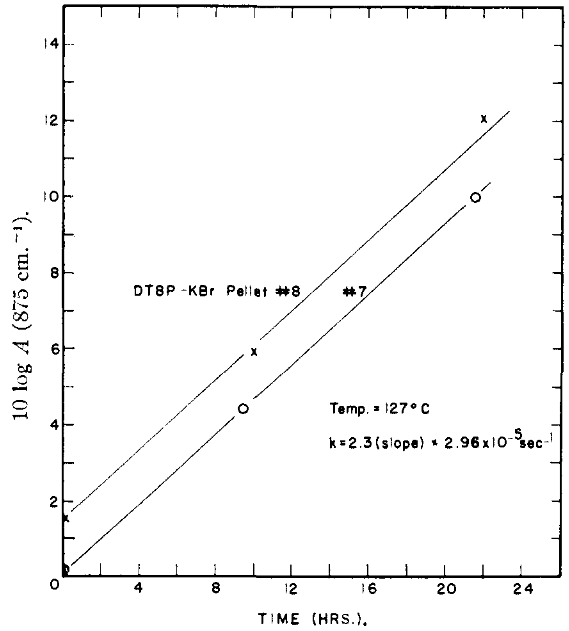

Fig. 2.—Kineticd ata on scission of the O–O bond of di-*t*-butyl peroxide in KBr pellets.

Plotted logarithmically against 1/*T*°K. (Fig. 3), these data give an activation energy of 38.0 kcal./mole

$$k = 1.45 \times 10^{16}\, e^{-38{,}000/RT}\ \text{sec.}^{-1}$$

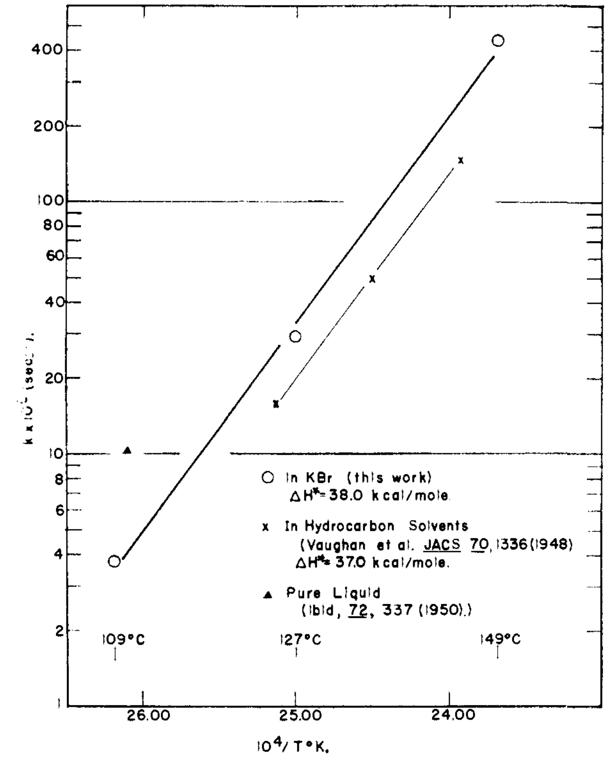

Fig. 3.—First-order rate constant for scission of the peroxide link in di-*t*-butyl peroxide.

For the gas phase decomposition, Raley, Rust and Vaughan[11] found that

$$k = 3.2 \times 10^{16}\, e^{-39{,}100/RT}\ \text{sec.}^{-1}$$

It appears that dispersion in KBr disks may be a convenient and safe technique for following the decomposition of unstable solids and liquids. We have followed the decomposition of di-*t*-butyl peroxide in this way—in ordinary ovens without steel and concrete barricades—up to temperatures 40° above those of previous studies on the pure liquid. Only a few milligrams are needed in an average

FIRST-ORDER RATE CONSTANT FOR SCISSION OF THE O–O BOND OF DTBP IN KBR PELLETS

Temp. (°C.)	$k \times 10^5$ (sec.$^{-1}$)
109	0.038
127	2.96
149	44.0

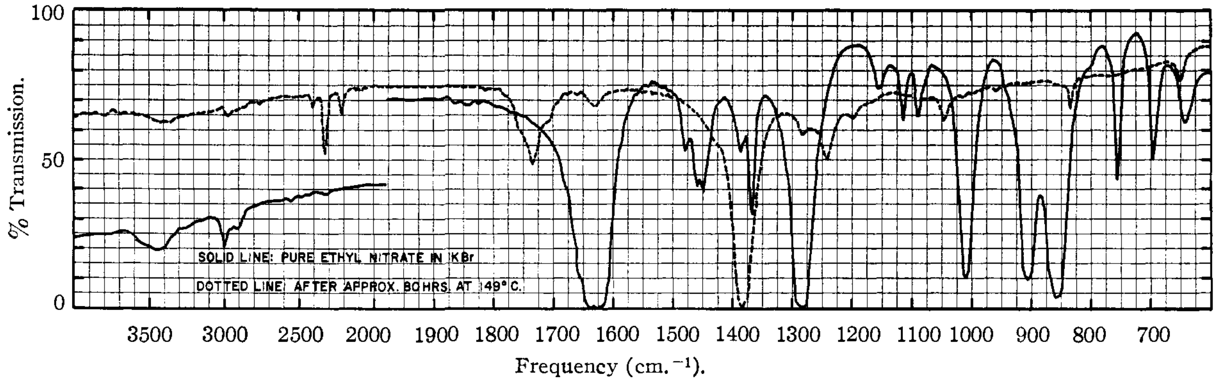

Fig. 4.—Spectra of ethyl nitrate and decomposition products in KBr.

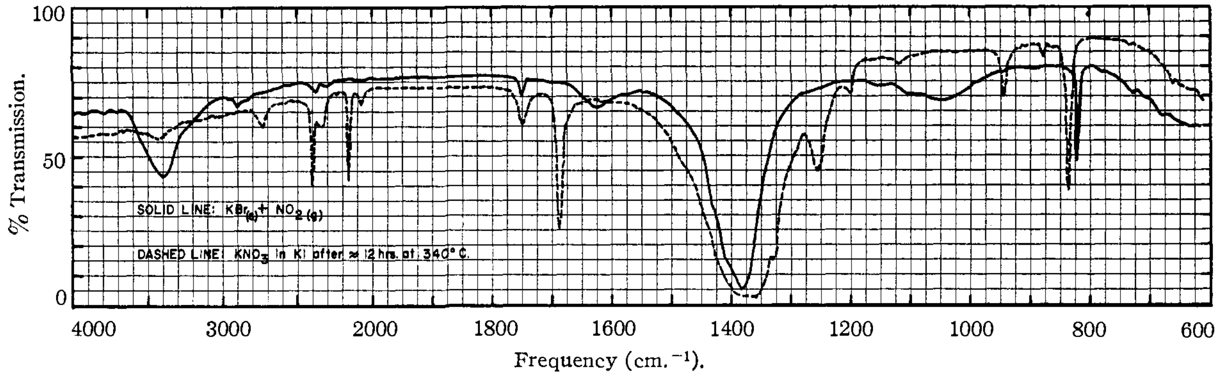

Fig. 5.—Formation and decomposition of NO_3^- in potassium halides.

disk (1.3 cm. × 0.25 cm.); a fairly complete kinetic study probably could be made with a gram, or less. The technique understandably works best when the kinetics are first order.

TABLE I

KINETIC DATA ON THE THERMAL DECOMPOSITION OF D-*t*-BUTYL PEROXIDE IN POTASSIUM BROMIDE PELLETS. ABSORBANCES OF THE 875 CM.$^{-1}$ BAND

DTBP-KBr pellet no.	Temp., °C.	Time, hr.	− log *A*
6	109	23.13	0.228
6	109	119.38	0.784
6	109	165.88	1.107
7	127	0.00	0.009
7	127	9.50	0.442
7	127	21.50	1.030
8	127	0.00	0.155
8	127	10.0	0.591
8	127	22.0	1.207
10	149	0.00 min.	0.283
10	149	30.00 min.	.603
10	149	60.00 min.	.806

Thermal Decomposition of Nitrate Esters in Potassium Halide Pellets.—Most striking in the decomposition of all nitrate esters in KBr was the appearance of a strong band at 1385 cm.$^{-1}$ (Fig. 4). The same band appears also in KCl and KI; but not in the spectra of heat treated films and smears of nitrocellulose. It corresponds closely to the principal absorption band of ionic nitrates (Fig. 5), and can be obtained quite easily by exposing pellets of KCl, KBr or KI to NO_2 at room temperature (Fig. 5). Accompanying the 1385 cm.$^{-1}$ band, but weaker, is a sharp spike at 835 cm.$^{-1}$, which we have found with all ionic nitrates.

These facts suggest that primary homolytic cleavage of the $RO-NO_2$ bond (reaction 1) in KX (X = Cl, Br or I) is followed by the reaction[13]

$$2NO_2 + KX = KNO_3 + [NOX] \qquad (3)$$

We have verified spectroscopically that NOX is formed at room temperature for X = Cl and Br. At higher temperatures (decomposition temperatures ranged from 120–190°), it would presumably exist largely as X_2 and nitric oxide[13]—although we have not seen the latter, owing perhaps to its small infrared extinction coefficient, or more likely, to its instability with respect to oxygen atom transfer, to form CO_2 (2350 cm.$^{-1}$) and CO (2170 cm.$^{-1}$) (Fig. 4).

Heterolytic cleavage of the $R-ONO_2$ bond to form NO_3^- directly might give R–X as a by-product. A search in the KBr region (400–800 cm.$^{-1}$) for the characteristic C–Cl and C–Br stretching frequencies gave no evidence of this.

Further evidence for homolytic $RO-NO_2$ cleavage, followed by reaction of NO_2 with the halide matrix (according to (3)), comes from the twin observations (i) that the observed first-order rate constant for the falling off of the nitrate ester bands of nitrocellulose (symmetrical stretch at 1280 cm.$^{-1}$, antisymmetrical stretch at 1650 cm.$^{-1}$) decreases markedly with time, suggesting some sort of interaction with the surrounding matrix; and

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[13] D. M. Yost and H. Russell, "Systematic Inorganic Chemistry", Prentice-Hall, Inc., New York, N. Y., 1946, p. 42.

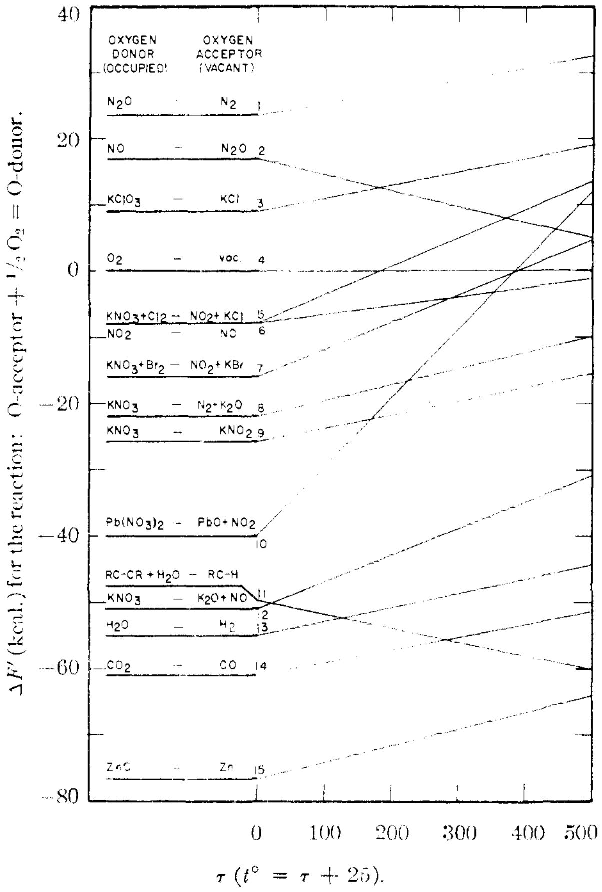

Fig. 6.—Oxygen levels. $\Delta F'(\tau) = \Delta F°(298) - \tau\Delta S°(298) \approx \Delta F°$ ($t° = \tau + 25$) for the reaction: oxygen-acceptor + $^1/_2$ O_2 = oxygen-donor. ($\Delta F'(\tau) = \Delta F°(\tau + 25)$ when $\Delta C_p° = 0$.)

(ii) that the rate of appearance of the 1385 cm.$^{-1}$ NO_3^- band is greatest in KI matrices and least in KCl, this being precisely the order of the rates of reaction of these halides with free NO_2. (This is also evidence against participation of atmospheric oxygen in the pellet production of NO_3^-, confirmed by heating several pellets *in vacuo*.)

It has been observed, also, that NO_3^- is itself an unstable intermediate, albeit a relatively long lived one. With nitrocellulose, which has no strong bands interfering at 1385 cm.$^{-1}$, the *yield* of inorganic nitrate (defined as the absorbance of the 1385 cm.$^{-1}$ band divided by the change in absorbance of the 1280 cm.$^{-1}$ band of nitrocellulose) decreased with increasing time in every observed case. Yields, in addition, are a function of the temperature and the matrix, being greater in KBr than in KCl at 122, 136, 156 and 186°, but least of all in KI at 186° (after one minute)—although the *production* of NO_3^- (Abs. at 1385 ÷ initial Abs. at 1280) was greatest in KI, as observed previously at room temperature.

Thermal Decomposition of NO_3^- in Potassium Halide Pellets.—In the absence of a good sink for left-over oxygen atoms, oxidizing agents such as NO_3^- are relatively stable. Anhydrous potassium nitrate, for example, is much more stable than aqueous nitric acid with respect to decomposition to nitric oxide and oxygen

$$2HNO_3(aq) = 2NO + 3/2\ O_2 + H_2O \qquad \Delta F°(298) = +36.6 \text{ kcal.} \quad (4)$$

$$2KNO_3(c) = 2NO + 3/2\ O_2 + K_2O \qquad \Delta F°(298) = +153.1 \text{ kcal.}$$

The $\Delta F°$ difference, 153.1 − 36.6 = 116.5 kcal., comes largely from the fact that water is a much better sink for oxygen than K_2O

$$2K^+(aq) + H_2O = K_2O + 2H^+(aq) \qquad \Delta F°(298) = +115.4 \text{ kcal.} \quad (5)$$

(This contrasts sharply with the relatively small unitary free energy[14,15] of solution of most ionic compounds, even insoluble ones such as barium sulfate (+16.6 kcal.)).

Anhydrous potassium chlorate, on the other hand, can lose oxygen relatively easily

$$KClO_3 = KCl + 3/2\ O_2 \qquad \Delta F°(298) = -28.3 \text{ kcal.} \quad (6)$$

showing (*cf.* 4) that Cl^- and NO_3^- are quite stable in KCl with respect to the alternative arrangement, $2NO + ClO_3^- + O^=$(as K_2O).

$$KClO_3 + 2NO + K_2O = 2KNO_3 + KCl \qquad \Delta F°(298) = -181.4 \text{ kcal.} \quad (7)$$

In assessing the relative stability of atomic configurations accessible to the NO_3^- + KX system, X a halogen, we have found it quite useful to characterize a rearrangement such as (7) as the transfer of oxygen atoms. We say that $KClO_3$ (going to KCl) is a better oxygen-donor than KNO_3 (going to NO + K_2O); that NO + K_2O (going to KNO_3) is a better oxygen-acceptor than KCl (going to $KClO_3$); or that oxygen atoms spontaneously leave the [$KClO_3$–KCl] level (written $KClO_3$ when occupied and KCl when vacant) for the [KNO_3– NO + K_2O] level (written KNO_3 when occupied and NO + K_2O when vacant). We get in this way the left side of Fig. 6.[16] (The corresponding levels in aqueous solution are displaced upward approximately + 115.4 kcal. per H_2O consumed per $^1/_2$ O_2.)

The best oxygen-donors appear by convention, like the best reducing agents in a table of oxidation potentials, on top at the left; the best oxygen-acceptors at the bottom on the right (Zn, CO and H_2 are included for comparison). Oxygen atoms tend to fall from upper-left to lower-right; in our example from level 3 to level 12. The square root of the oxygen partial pressure above level 3 is $e^{\Delta F_3'/RT}$, that above level $12 P_{NO}^{-2/3} e^{\Delta F_{12}'/RT}$, these two escaping tendencies being equal at equilibrium. Reaction 3 (for X = Br, and NOBr dissociated to NO + Br_2) corresponds to the tumbling of oxygen atoms from level 6 to 7.

Figure 6 has been extended off to the right in the following manner. $\Delta F°(T) = \Delta H°(T) - T\Delta S°(T) \approx \Delta H°(298) - T\Delta S°(298) = \Delta F°(298) - (T - 298)\Delta S°(298) = \Delta F°(298) - \tau\Delta S°(298)$, $\tau = t° - 25$. What has been plotted against τ in Fig. 6 is this quantity $\Delta F°(298) - \tau\Delta S°(298)$, abbreviated $\Delta F'(\tau)$. $\Delta F'(\tau)$ is precisely equal to

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[14] R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., New York, N. Y., 1953, Chap. 5.

[15] H. A. Bent, *J. Phys. Chem.*, **60,** 123 (1956).

[16] *Cf.* ref. 14, Chap. 7, Section 69.

ΔF° (25° above τ) when $\Delta C_p{}^\circ$ for the reaction oxygen-acceptor + $^1/_2$ O_2 = oxygen-donor is zero. When $\Delta C_p{}^\circ \neq 0$, ΔH° and ΔS° 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.

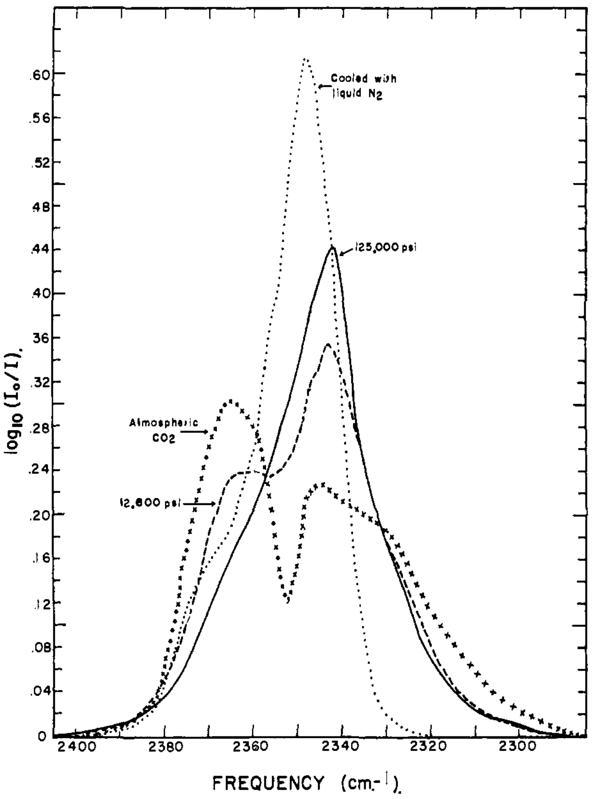

Fig. 7.—Spectra of CO_2 at high pressures.

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MINNEAPOLIS 14, MINN.

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES, BROWN UNIVERSITY]

The Exchange Behavior of Monosubstituted Peroxides

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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.

(3) (a) R. S. Winter and H. V. A. Briscoe, THIS JOURNAL, **73**, 496 (1951); (b) P. Baertschi, *Experientia*, **7**, 215 (1951); (c) J. Halperin and H. Taube, THIS JOURNAL, **74**, 380 (1952); (d) M. Dole, G. Muchow, De F. P. Rudd and C. Comte, *J. Chem. Phys.*, **20**, 961 (1952).

(4) (a) I. M. Kolthoff and I. K. Miller, THIS JOURNAL, **73**, 3055 (1951); (b) R. L. Eager and K. J. McCallum, *Can. J. Chem.*, **32**, 692 (1954); (c) P. C. Riesebos and A. H. W. Aten, Jr., THIS JOURNAL, **74**, 2440 (1952); (d) H. Elkeles and C. Brosset, *Svensk. Kem. Tidskr.*, **65**, 26 (1953).