Alkylperoxy and Alkyl Radicals. 5. Infrared Spectra and Ultraviolet Photolysis of t-$C_4H_9O_2$ Radicals in Argon plus Oxygen Matrices

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tert-Butyl radicals formed by the pyrolysis of azoisobutane were isolated in matrices of Ar + 10% $^{16}O_2$ and Ar + 5% $^{16}O_2$ + 5% $^{18}O_2$. IR spectra of the resulting trapped species were obtained before and after irradiation of the matrices with a medium-pressure Hg arc lamp. In the 1200–200-cm^{-1} spectral range, nine absorption bands were observed and assigned to the *tert*-butylperoxy radical. A summary of the known vibration frequencies assigned to primary, secondary, and tertiary alkylperoxy radical centers is presented.

Introduction

IR matrix isolation spectra for CH_3O_2, $CH_3O_4CH_3$, $C_2H_5O_2$, $C_2H_5O_4C_2H_5$, i-$C_3H_7O_2$, and i-C_3H_7 were reported in the first four papers of this series.[1-4] As noted in the earlier papers, until the current studies, little was known about the IR spectra of the alkylperoxy radicals, species that are important in atmospheric chemistry[5] and low-temperature oxidation processes.[6] In this final paper of the series, we report the IR spectrum of the *tert*-butylperoxy radical in the 1200–200-cm^{-1} range. The data are not as extensive as those for the other alkylperoxy radicals studied but, when taken with the previous findings, provide a consistent picture for a vibrational frequency assignment for the *tert*-butylperoxy radical center.

Experimental Section

The matrix isolation cryostat and molecular beam pyrolysis tube furnace assembly used in this study have been described previously.[7] *tert*-Butyl radicals were produced by the pyrolysis of azoisobutane. To form *tert*-butylperoxy radicals, *tert*-butyl radicals were allowed to react during the trapping process with Ar matrices containing 10% O_2. Matrix deposition times varied from 20 to 70 h. Absolute values of the radical matrix gas dilution ratios were not known. Experiments were run at sufficient matrix dilution to minimize dimerization of reactive species.

Azoisobutane was synthesized according to a procedure described in the literature.[8] A 50% mixture of unscrambled oxygen isotopes, $^{18}O_2$ + $^{16}O_2$, was obtained from Prochem. The Ar matrix gas and $^{16}O_2$ were Matheson Research Grade. Reference IR matrix spectra were generated for the following materials: $(t$-$C_4H_9)_2N_2$, i-C_4H_{10}, i-C_4H_8, i-C_4H_9OH, and C_8H_{18} (2,2,3,3-tetramethylbutane). The latter four materials, stated purities ≥98%, were used as supplied.

On occasion, matrices were subject to irradiation from a medium-pressure 500-W Hg arc lamp for periods of up to 16 h. IR spectra in the 4000–200-cm^{-1} range were recorded on a Perkin-Elmer Model 273 spectrophotometer. Reported frequencies are accurate to ±2 cm^{-1}.

Results and Discussion

tert-Butyl Radical Spectra. Preliminary experiments established the conditions for the effective pyrolysis of azoisobutane using pure Ar for trapping the decomposition products. At a temperature of $\simeq$270 °C, essentially all the azoisobutane was pyrolyzed; the only stable products identified, in addition to small amounts of H_2O, CO_2, and CO, were isobutylene and isobutane. At the matrix dilutions used, no evidence was found for the formation of 2,2,3,3-tetramethylbutane. Additional absorption bands found in the spectrum could readily be assigned to the *tert*-butyl radical by comparing them to data reported in the literature for this radical isolated in an Ar matrix.[9]

tert-Butylperoxy Radical Spectra. A series of experiments was performed in which *tert*-butyl radicals were isolated in Ar matrices containing either 10% $^{16}O_2$ or 5% $^{16}O_2$ + 5% $^{18}O_2$. The major reaction expected in the matrix experiments, based on the known chemistry of the system at ambient temperature[10] and similar experiments with CH_3, C_2H_5,[3] and i-C_3H_7[2] radicals is

$$t\text{-}C_4H_9 + O_2 \rightarrow t\text{-}C_4H_9O_2$$

Subsequent self-reaction of t-$C_4H_9O_2$ radicals at ambient temperature reportedly produces the stable products acetone, *tert*-butyl alcohol, *tert*-butyl hydroperoxide, methanol, and formaldehyde.[10] None of these products was expected under the experimental conditions used in this study since matrix dilutions were sufficiently high to preclude bimolecular peroxy radical collisions. Indeed, there was no evidence that acetone, *tert*-butyl alcohol, methanol, or formaldehyde were present in the "as-deposited" matrices.

The spectra obtained by allowing *tert*-butyl radicals to react with oxygen-containing Ar matrices clearly showed the presence of isobutane and isobutylene, a complete absence of any absorption bands attributable to *tert*-butyl radicals, and the appearance of a number of new absorption bands. In the 2700–3150- and 1300–1500-cm^{-1} spectral ranges, it was clear that many of the absorption bands attributable to i-C_4H_{10} and i-C_4H_8 were overlapped by those of other species. In the 1200–200-cm^{-1} spectral range, where the density of absorption bands due to i-C_4H_{10} and i-C_4H_8 was relatively low, the presence of the new absorption features was more clearly defined. For this reason, only the new spectral features occurring in the 1200–200-cm^{-1} range are discussed.

The relevant spectra for matrices containing 10% $^{16}O_2$ and 5% $^{16}O_2$ + 5% $^{18}O_2$ (unscrambled) are shown in Figure 1. Curves A and C are spectra of the as-deposited matrices containing $^{16}O_2$ and $^{16}O_2$ + $^{18}O_2$, respectively; curves B and D are the spectra after photolysis with a medium-pressure Hg arc lamp of the as-deposited matrices shown in curves A and C. In previous studies, Hg arc photolysis of matrices containing CH_3O_2,[1] $C_2H_5O_2$,[4] and i-$C_3H_7O_2$[3] radicals resulted in complete destruction of the radicals. Concomitantly, absorption bands attributable to CO_2 and H_2O intensified and many new absorption bands appeared. In all three cases, a very strong broad absorption band in the 1700–1740-cm^{-1} spectral range was reasonably assigned to a carbonyl vibration

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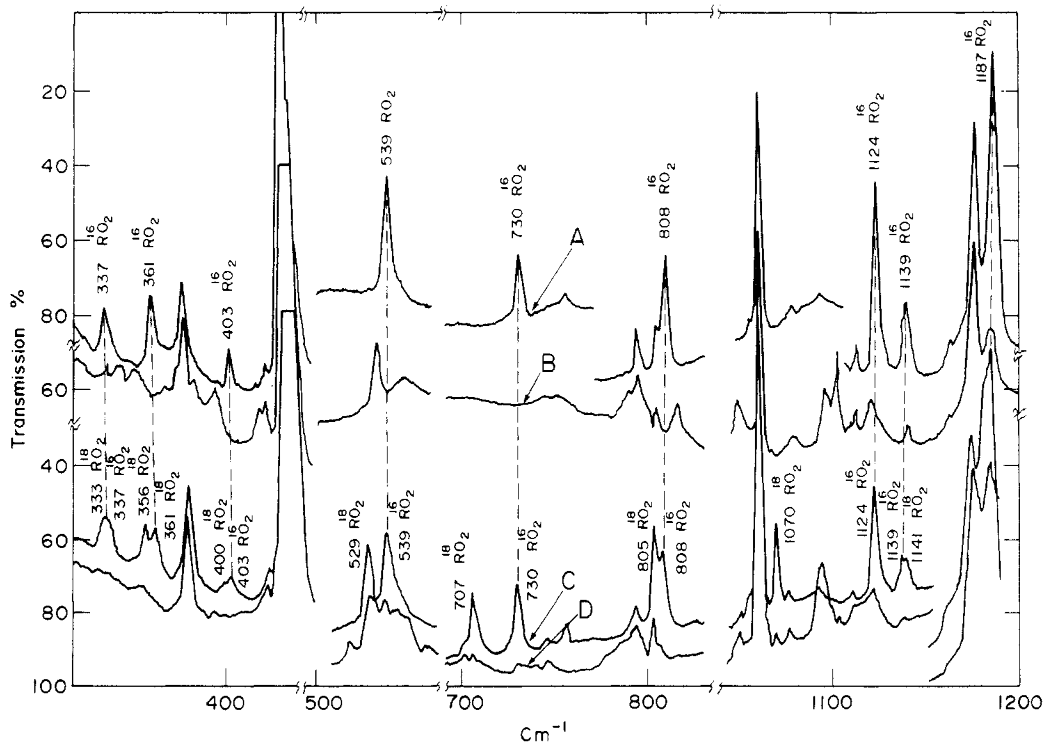

Figure 1. IR spectra (1200–300 cm^{-1}) of reaction products formed from the interaction of t-C_4H_9 radicals and a matrix gas of Ar + 10% $^{16}O_2$ (curve A) and Ar + 5% $^{16}O_2$ + 5% $^{18}O_2$ (curve C). Curves B and D were recorded after the matrices in A and C were irradiated with a medium-pressure Hg arc for 16 h.

TABLE I: Tentative Vibrational Frequency Assignments (1200–200 cm^{-1}) for t-$C_4H_9{}^{16}O_2$ and t-$C_4H_9{}^{18}O_2$ Radicals

approx vibration mode	frequencies, cm^{-1} t-$C_4H_9{}^{16}O_2$	t-$C_4H_9{}^{18}O_2$	$^{16}\nu/^{18}\nu$
CH_3 rock	1187	1184	1.003
CH_3 rock	1139	1141	0.998
O–O stretch	1124	1070	1.051
C–C stretch	808	805	1.004
C–O stretch	730	707	1.033
(C_3)–C–O–O out-of-phase bend	539	529	1.019
skeletal C bend	403	400	1.008
(C_3)–C–O–O in-phase bend	361	356	1.014
skeletal C bend	337	333	1.012

frequency perturbed by hydrogen bonding. In the present study, Hg arc photolysis resulted in marked increases in the intensity of the H_2O and CO_2 absorption bands. In addition, a strong broad absorption band appeared with a doublet structure peaked at 1738 and 1718 cm^{-1} (10% $^{16}O_2$) and a quartet structure peaked at 1738, 1704, 1718, and 1686 cm^{-1} (5% $^{16}O_2$ + 5% $^{18}O_2$). Photolysis of CH_3O_2 and i-$C_3H_7O_2$ radicals resulted in carbonyl absorption bands which were assigned to CH_2O and $(CH_3)_2CO$, respectively. The corresponding frequencies were reported at 1736 ($CH_2{}^{16}O$), 1704 ($CH_2{}^{18}O$), 1716 ($CH_3C^{16}OCH_3$), and 1688 cm^{-1} ($CH_3C^{18}OCH_3$). Considering the broadness of these absorption bands and their sensitivity to hydrogen-bonding effects, the frequencies observed in the present study in this spectral region could reasonably indicate the presence of both CH_2O and $(CH_3)_2CO$ in the matrix after photolysis. The detailed mechanism for the formation of the carbonyl compounds from their precursor peroxy radicals on photolysis in the matrix is not known. It is noted that the carbonyl compounds formed on photolysis of CH_3O_2 and i-$C_3H_7O_2$ in matrices are the same as those formed in the self-reactions of these radicals. Both CH_2O and $(CH_3)_2CO$ are formed in the self-reaction of t-$C_4H_9O_2$ radicals.[10] The formation of these carbonyl compounds on photolysis of matrices in the present study is consistent with t-$C_4H_9O_2$ as the precursor species, assuming it behaves in the same way as CH_3O_2 and i-$C_3H_7O_2$ on both photolysis and self-reaction.

On the basis of the above observations, absorption bands present in the as-deposited matrices that were bleached on Hg arc photolysis were assigned to the t-$C_4H_7O_2$ radical. These absorption bands are designated by $R^{16}O_2$ and $R^{18}O_2$ in Figure 1. The frequencies associated with these bands, their isotopic vibration frequency ratios, and tentative vibrational mode assignments are presented in Table I. In making the assignments, a nonlinear C–O–O moiety was assumed, with a radical symmetry C_s, in which all vibrational modes are IR active. Approximate values were estimated for the isotopic frequency ratios $^{16}O/^{18}O$ associated with the O–O stretch, 1.06; C–O stretch, 1.025; and C–O–O bend, 1.025. These frequency ratios, when taken in conjunction with previous vibrational assignments for alkylperoxy radicals,[1–4] allow the assignment of the peroxy radical oxygen-mass-dependent vibrational modes as indicated in Figure 1. The choice of 361 cm^{-1} rather than 337 cm^{-1} (t-$C_4H_9{}^{16}O_2$) for the (C_3)–C–O–O in-phase bending mode is arbitrary. The reverse assignment would be equally plausible. The remaining frequencies were assigned by analogy with those reported for t-C_4H_9[9] and hydrocarbons in general.[11]

TABLE II: Vibration Frequencies (cm^{-1}) of the O–O and C–O Stretching and C–O–O Bending Modes of Some Alkylperoxy Radicals

radical	O–O stretching mode $^{16}O_2$	$^{18}O_2$	$^{16}\nu/^{18}\nu$	C–O stretching mode $^{16}O_2$	$^{18}O_2$	$^{16}\nu/^{18}\nu$	C–O–O bending modes $^{16}O_2$	$^{18}O_2$	$^{16}\nu/^{18}\nu$
CH_3O_2[1]	1112	1056	1.053	902	880	1.025	492	476	1.034
$C_2H_5O_2$[4]	1112	1065	1.044	838	[a]		499	484	1.030
i-$C_3H_7O_2$[3]	1101	1059	1.040	789	770	1.025	515	502	1.026
t-$C_4H_9O_2$	1124	1070	1.051	730	707	1.033	539	529	1.019
CF_3O_2[12,13]	1098	1038	1.057	870	854	1.018	692 (448)	678 (440)	1.020 (1.018)

[a] Not reported due to absorption band overlapping problems.

The data presented in Table II summarize current results on vibration frequency assignments associated with primary, secondary, and tertiary alkylperoxy radical centers. Immediately apparent is the constancy of the O–O stretching mode frequency, a value of 1111 ± 1.2% cm^{-1}, encompassing the range of values found in the five peroxy radicals studied. The O–O stretching frequencies of hydrogenated and perfluorinated alkyl peroxides fall in the 700–890-cm^{-1} range,[14,15] values distinctly different from those found in the alkylperoxy radicals. The C–O stretching frequencies of the alkylperoxy radicals show considerable variation, decreasing overall by $\simeq$19%, in the order primary > secondary > tertiary. This is opposite to the variation found for C–O stretching frequencies in aliphatic alcohols which cover the range from 1000 (primary) to 1200 cm^{-1} (tertiary).[11] In the hydrogenated alkylperoxy radicals, the C–O–O bending frequencies increase overall by $\simeq$10%, in the order primary < secondary < tertiary. The trifluoromethylperoxy radical C–O–O bending mode does not appear to fit this trend. In this case, however, a normal coordinate analysis of the radical clearly showed that considerable mixing of the carbon–fluorine and carbon–oxygen vibrational modes occurred.[13] In the 692–448-cm^{-1} ($CF_3{}^{16}O_2$) range, a total of four vibration frequencies were assigned to the radical that exhibited marked $^{16}O_2$ and $^{18}O_2$ isotope effects. Assignment of any of these frequencies specifically to the C–O–O bending mode was thus somewhat arbitrary.

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Registry No. Ar, 7440-37-1; $^{16}O_2$, 7782-44-7; $^{18}O_2$, 32767-18-3; *t*-$C_4H_9O_2$, 3395-62-8; H_2O, 7732-18-5; CO_2, 124-38-9; CH_2O, 50-00-0; $(CH_3)_2CO$, 67-64-1; *tert*-butyl radical, 1605-73-8; isobutylene, 115-11-7; isobutane, 75-28-5.

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Transient Resonance Raman Spectra of Benzophenone and Its Four Isotopic Analogues in the Lowest Excited Triplet State

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Transient resonance Raman spectra of T_1 benzophenone (T_1 BP) and its four isotopic analogues in carbon tetrachloride solutions were measured. Vibrational assignments of eight T_1 bands have been made on the basis of the observed isotopic frequency shifts. The assignments clarified the following three points concerning the structure of T_1 BP in solution. (1) The CO bond order in T_1 BP is much lower than that in the ground-state benzophenone (S_0 BP). The CO stretching frequency in T_1 is found to be 1222 cm^{-1}, whereas the corresponding value in S_0 is 1665 cm^{-1}. The former frequency indicates a single-bond-like character of the CO bonding in the T_1 state. (2) Vibrational frequencies of several ring modes show marked downshifts in going from S_0 to T_1. This suggests the delocalization of the π^* electron into the ring part. (3) The assignment (1302 cm^{-1}) of the symmetric C–phenyl stretch mode in the $T_1 \leftarrow S_0$ absorption spectrum is questioned. According to the present assignment, the frequency of this mode ($\sim$1100 cm^{-1}) is slightly lower than that in the ground state (1150 cm^{-1}). The simple quantum chemical picture of T_1 BP, which predicted the increase of the C–phenyl bond order with the $\pi^* \leftarrow$ n excitation, should therefore be reconsidered.

1. Introduction

Benzophenone in the lowest excited triplet state (T_1 BP) is known to be highly electrophilic and plays important roles in a variety of photochemical reactions as a key intermediate. The photoreduction by amines is a prototypical example of such reactions. In this reaction, the benzophenone ketyl and the amine cation radical are formed as a result of the abstraction of an amine hydrogen by T_1 BP. The detailed mechanism of the hydrogen abstraction was first discussed by Cohen et al.[1] According to the scheme proposed by these authors, the electron transfer from amine to T_1 BP initiates the reaction. The resultant solvent-separated ion pair evolves, by electrostatic attraction, to form a contact ion pair which facilitates the transfer of a proton from amine to T_1 BP. This scheme was subsequently confirmed by nano- and picosecond laser photolysis studies.[2-4] The high reactivity of T_1 BP may be best manifested by the fact that the hydrogen abstraction quantum yield can be as high as unity for primary amines. On the other hand, the ground-state benzophenone (S_0 BP) does not react with amines under ordinary conditions. The difference in the reactivity is explainable in terms of the difference in the electron density distribution between T_1 BP and S_0 BP. Such a drastic change in the reactivity and hence in the electron density distribution should also be reflected in the molecular structure. In other words, an inherent correlation is expected between the reactivity and the molecular structure through the electron density distribution.

The analysis of the vibrational spectrum gives unique information about the molecular structure. However, the application of this technique to T_1 BP was very limited. The only existing vibrational data for T_1 BP are those obtained from the vibrational structure of the $T_1 \leftarrow S_0$ absorption spectrum of crystal at liquid helium temperature.[5,6] A few low-frequency bands as well as two fundamentals at 1219 and 1529 cm^{-1} were observed. The latter two were assigned to the CO and ring stretches, respectively. Although these data are of high enough quality to discuss the character of T_1 BP in crystal at low temperature, they are not directly correlated to the reactivity which is measured in solution

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