Tetrahedron Vol. 38, No. 2, pp. 257 to 260, 1982
Printed in Great Britain.

0040–4020/82/020257–04$03.00/0
Pergamon Press Ltd.

PHOTOCHEMICAL STUDIES ON THE TERTIARY BUTYL RADICAL ISOLATED IN ARGON MATRICES

J. PACANSKY,* J. S. CHANG and D. W. BROWN
IBM Research Laboratory, San Jose, CA 95193, U.S.A.

(*Received in U.S.A.* 18 *May* 1981)

Abstract—The t-Bu radical was isolated in an argon matrix and exposed to short wavelength UV light. Two major phoroproducts were observed using IR spectroscopy: the first, isobutylene, was formed by cleavage of a βCH bond; the second was the i-Bu radical which could have been formed by a photoisomerization, or recombination of a H atom with isobutylene.

Photochemical studies on organic free radicals are rare. The studies that have been made are usually carried out using ESR spectroscopy to follow the reaction.[1] This has advantages, but suffers from being only capable of observing other open shell species photochemically produced. Another handicap is due to the sensitivity of the method the particular photochemical reaction observed by an ESR technique may be only a very minor photochemical reaction.

In this report, photochemical studies are reported on matrix isolated t-Bu radicals. Since the reaction is followed by IR spectroscopy, the macroscopic photochemical reactions are observed which involve both closed shell and open shell species. The results clearly show that photoexcitation of an alkyl radical induces scission of a βCH bond to form an alkene and, possibly, a photoisomerization to another alkyl radical via a (1,2)-H migration. Precedence is found for the βCH scission reaction in the thermal chemistry of alkyl radicals, but not for the isomerization reaction; this is presumably due to the high activation energy for the (1,2)-H migration.

EXPERIMENTAL

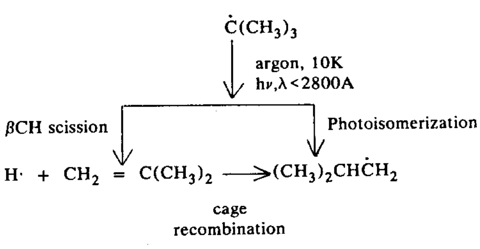
The t-Bu radical was produced by the flash vacuum pyrolysis of a gaseous mixture of azoisobutane in argon (concentration: 1/300) at 700 ± 50K. A complete account of the pyrolysis experiments providing evidence for the production and existence of the radical in rare gas matrices has been given.[2] The photochemical studies reported here use this same method to produce the radical in argon matrices.

The UV light source used to irradiate the tertiary butyl radical was an EIMAC VIX-150 watt xenon high-pressure lamp with a total output of 40 mW in the $\lambda < 2500$A region. Spectral regions of interest in the UV were isolated using standard Corning glass filters.

RESULTS AND DISCUSSION

Figure 1 contains the IR spectrum of the tertiary Bu radical along with isobutylene, the gas phase thermal product of the radical (very small amounts of isobutane and 2,3-tetramethylbutane are also present). The IR spectrum of isobutylene isolated in an argon matrix is shown in Fig. 2 in order to clearly identify this species in Fig. 1. Exposure of the argon matrix to UV light containing the t-Bu radical had no effect until wavelengths shorter than 2800A were used. This agrees with the UV absorption spectrum for the t-Bu radical reported by Parkes and Quinn,[3] who established that the radical has a broad weak absorption extending to 2700A in the gas phase. Upon exposure of the matrix to the full output of the 150 watt high-pressure xenon lamp, the IR spectrum of the t-Bu radical simultaneously decreased with an increase in absorption for isobutylene, as shown by the change in intensity of the isobutylene band at 434 cm^{-1} in Fig. 3. The three new bands at 3115, 3023 and 550 cm^{-1} also shown in Fig. 3 were unequivocally identified as three characteristic absorptions for the i-Bu radical by obtaining the IR spectrum for the latter radical by photolysis of the following matrix isolated peroxide: $(CH_3)_2CHCH_2CO_2O_2CCH_2CH(CH_3)_2$. This work is discussed at length in another report;[4] however, it is pertinent to state here that the absorptions at 3115 and 3023 cm^{-1} are due to the stretching motions of the αCH bonds, while the band at 550 cm^{-1} is due to the pyramidal bending mode of the primary radical center. These absorptions have been successfully established as characteristic features for primary alkyl radicals in other reports.[2,4,5]

The two photochemical paths observed for the t-Bu radical in an argon matrix are summarized below in Scheme 1. The photochemical cleavage of the βCH bond to form isobutylene is analogous to the thermal βCH bond cleavage. Since the activation energy for the thermal reaction is only 43.6 kcal/mole,[6] the photochemical βCH bond cleavage is not a surprise. The photoisomerization of the t-Bu radical to form the thermodynamically less stable i-Bu radical, however, is an interesting path for the radical to take. Although thermodynamically the radicals have very close enthalpies of formation ($\Delta H_f{}^0 = 14$ and 10.5 kcal/mol for the i-Bu[7] and t-Bu[2] radicals), the isomerization proceeds to the primary radical. This is most likely due to a difference in the electron absorption



Scheme 1.

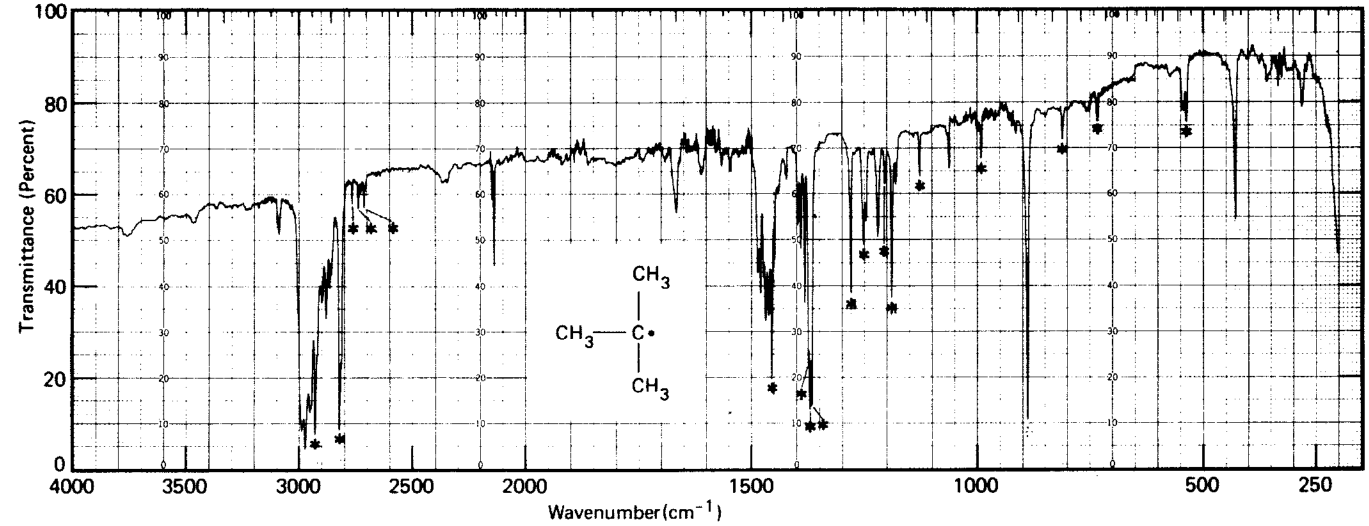


Fig. 1. The IR spectrum of azo-isobutane isolated in an argon matrix after flash vacuum pyrolysis. The following bands (marked with an *) are assigned to the tertiary butyl radical: 2931, 2825, 2769, 2743, 2716, 1455, 1375, 1371, 1367, 1279, 1252, 1205, 1189, 1126, 992, 811, 733 and 541 cm^{-1}.

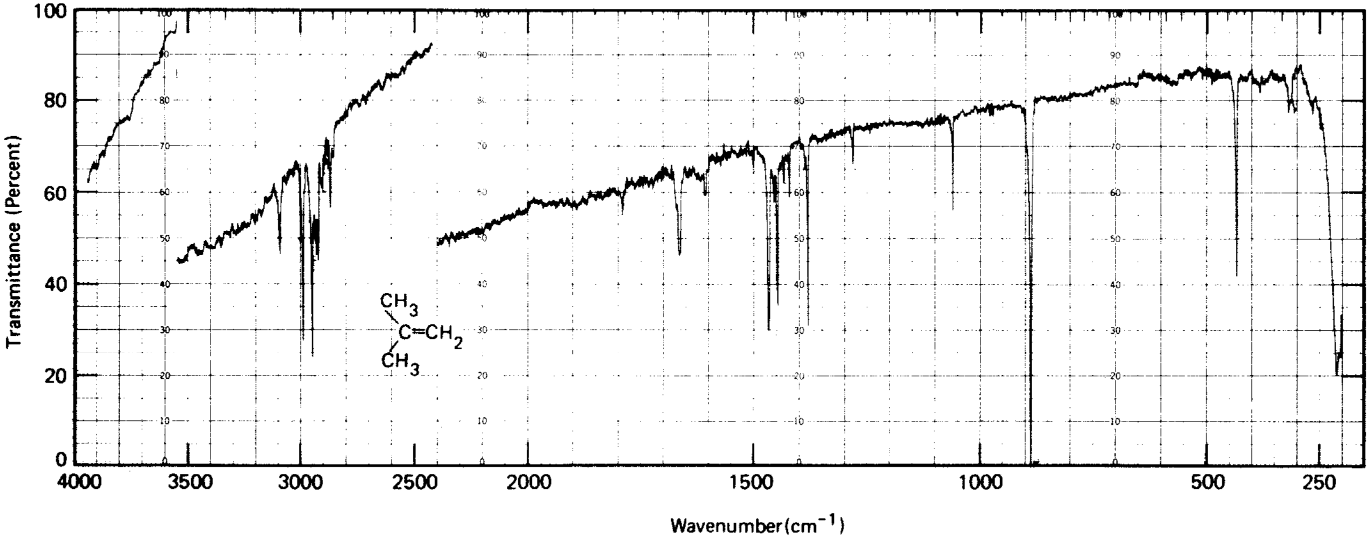


Fig. 2. The infrared spectrum of isobutylene in an argon matrix (concentration: 1/500; T = 10K).

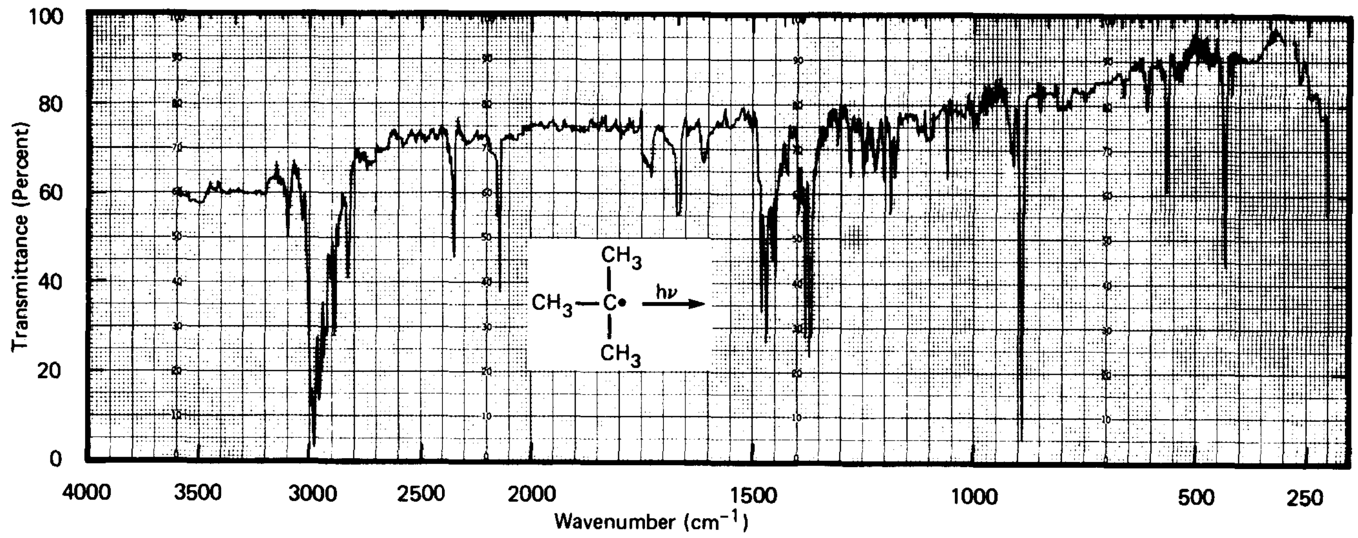


Fig. 3. The infrared spectrum of the tertiary butyl radical after irradiation with the full output of a high-pressure Xenon lamp.

between a primary and tertiary alkyl radical. Parkes and Quinn[8] observed that the electronic absorption spectra of the Me radical shifted to longer wavelengths as more Me groups were substituted for hydrogens. As a consequence, it is reasonable to expect that primary alkyl radicals have a shorter UV wavelength absorption than tertiary alkyl radicals. Photochemical studies on the Et and i-Pr radicals support this claim.[9] On this basis the t-Bu radial could be photochemical driven to the i-Bu radical which is a primary alkyl radical with shorter wavelength absorption in the UV.

The possibility that the isomerization to the i-Bu radical is due to a recombination reaction of an H atom with isobutylene which were photochemically produced in the same cavity (cage effect) cannot be eliminated. This possibility always exists in solid state photochemical reactions.[1] It should be noted, however, that even though H atoms are being produced by light, no increase in the IR absorption of isobutane was observed. This eliminates recombination of H atoms with t-Bu radicals. The disproportionation reaction of H atoms with t-Bu radicals should be favored and the possibility of some isobutylene being formed by this route is plausible.

CONCLUSION

Photochemical matrix isolation studies on the t-Bu butyl radical reveal that at least two major photoproducts are produced. The first involves a βCH scission to form an H atom and isobutylene; the second product is the i-Bu radical, which could be formed either by a photoisomerization or a cage recombination reaction.

REFERENCES

[1] M. Ya. Mel'nikov and N. V. Fok, *Russian Chemical Reviews* **49**, 131 (1980).
[2] J. Pacansky and J. S. Chang, *J. Chem. Phys.* **74**, 5539 (1981).
[3] D. A. Parkes and C. P. Quinn, *Chem. Phys. Letters* **33**, 483 (1975).
[4] J. Pacansky, D. W. Brown and J. S. Chang, *J. Phys. Chem.* **85**, 2562 (1981).
[5] J. Pacansky, D. E. Horne, G. P. Gardini and J. Bargon, *Ibid.* **81**, 2149 (1977).
[6] J. A. Kerr and A. C. Lloyd, *Quart. Rev.* **22**, 549 (1968).
[7] J. A. Kerr, *Chem. Rev.* **66**, 465 (1966).
[8] D. A. Parkes and C. P. Quinn, *J. Chem. Soc.* Faraday Trans. I **72**, 1952 (1976).
[9] J. Pacansky and H. Coufal, *J. Chem. Phys.* **72**, 3298 (1980); **71**, 2811 (1979).