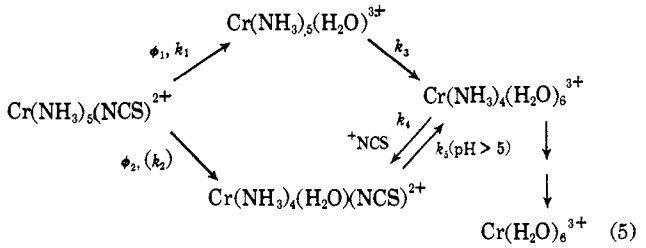

(5)

becomes noticeable at pH's as low as 5. Quite possibly the mechanism is one involving the formation of a hydroxy complex; it could be quite analogous to the counter base mechanism that has been proposed and largely accepted for the base hydrolysis of Co(III) acidoammine complexes.[37] Apparently, then, ammonia coordinated to Cr(III) is only very weakly acidic, and in order for the counter base mechanism to become important the more acidic coordinated water is required.

Acknowledgments. These investigations have been supported in part by Contract AT(11-1)-113 between the University of Southern California and the U. S. Atomic Energy Commission. In addition, E. Z. wishes to thank the National Science Foundation for assistance through Grant Gp-5725 and also the National Research Council of Italy.

Primary Quantum Yields in Photodissociation of Isopropyl Nitrite

Barbara E. Ludwig and G. R. McMillan

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received August 16, 1968*

Abstract: Illumination of isopropyl nitrite in the banded region at 3660 Å results in formation of isopropoxy radicals and nitric oxide with a primary quantum yield of 0.36 at 26°, inconsistent with the usual assumption that the primary yield is unity in nitrite photolysis. The *cis* and *trans* conformers apparently decompose with the same quantum efficiency. The primary yield for photodetachment of HNO or NOH is less than 0.06 and probably near zero. Excitation of the $^1(n,\pi^*)$ state with a few quanta in the terminal N=O stretching vibration leads to no more efficient decomposition than does excitation of the vibrationless state. On the basis of observed changes in the product distribution, this is not due to vibrational deactivation before decomposition.

The principal photodissociative process for simple alkyl nitrites at all wavelengths so far studied is a scission of the RO–NO bond to form an alkoxy radical and nitric oxide.[1] The primary quantum yield of this process is generally assumed to be unity,[2] but only for *t*-butyl nitrite[3] has the primary yield been measured in the banded region lying between 3200 and 4000 Å. A molecular split of the type $R_2CHONO + h\nu \rightarrow R_2CO + HNO$ (or NOH) has often been suggested, but Calvert and Pitts conclude that no unambiguous evidence is available on its importance.[4] The photolysis of isopropyl nitrite was studied to test the assumption of unit quantum efficiency for photodissociation; to determine the importance of the photodetachment of HNO; to try to detect differences, if any, in the photochemistry of the *cis* and *trans*-nitrite rotamers; and to test for coupling between excited vibrational levels in the (n,π^*) state and the decomposition mode. Photolysis of isopropyl nitrite has been previously studied both in the vapor phase and in solution.[5]

Experimental Section

Isopropyl nitrite was prepared by reaction of isopropyl alcohol with nitrous acid. The product was treated with anhydrous K_2CO_3 and mercury, distilled at atmospheric pressure, and stored at −78° on the vacuum line. Nitric oxide from the Matheson Co. was passed over silica gel cooled to −78° and finally fractionally distilled on the vacuum line. All illuminations were carried out in a quartz vessel of diameter 5 cm and volume 240 cm³. The Osram XBO 150 high-pressure xenon lamp was used in conjunction with a Bausch and Lomb grating monochromator. A Hanovia 673A medium pressure mercury arc was used with two filter systems to isolate 3660-Å radiation. The first filter system consisted of a 10-cm optical path of a 5 g/100 ml aqueous solution of $CuSO_4 \cdot 5H_2O$, followed by 1 cm of a 0.01 g/100 ml aqueous solution of 2,7-dimethyl-3,6-diazocyclohepta-1,6-diene perchlorate, and 0.5 cm of Corning glass 7-37. The transmission and stability of this filter have been recorded.[6] The second filter system consisted of the Corning glass 7-37 alone. Quantum yields were based on light intensities measured with the potassium ferrioxalate actinometer. The intensities were checked by measuring the quantum yield of nitrogen in photolysis of azomethane vapor. The yield was 1.05;

(1) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 480.
(2) P. Kabasakalian and E. R. Townley, *J. Amer. Chem. Soc.*, **84**, 2711 (1962); M. Akhtar, *Advan. Photochem.*, **2**, 263 (1964); R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 236; ref 1, p 481.
(3) G. R. McMillan, *J. Phys. Chem.*, **67**, 931 (1963).
(4) Reference 1, p 482.
(5) H. W. Thompson and F. S. Dainton, *Trans. Faraday Soc.*, **33**, 1546 (1937); P. Tarte, *Bull. Soc. Roy. Sci. Liege*, **22**, 226 (1953); P. Kabasakalian, E. R. Townley, and M. D. Yudis, *J. Amer. Chem. Soc.*, **84**, 2718 (1962).
(6) Reference 1, pp 734–735.

Table I. Quantum Yields in Photolysis of Isopropyl Nitrite

Wavelength isolation[a]	Wavelength, Å	Temp, °C	Pressure, mm i-C_3H_7ONO	Pressure, mm NO	$10^{-12}I_a$, quanta/(ml sec)	Time, hr	$\Phi_{CH_3COCH_3}$	Φ_{CH_3CHO}
I	3660	26	3.6	39	0.96	12	0.067	0.026
			3.9	32	1.00	12	0.066	0.035
			9.7	12	1.78	12	0.056	0.033
			9.7	40	1.98	12	0.059	0.024
			11.1	0	2.12	12	0.066	0.029
			12.1	0	2.24	12	0.051	0.022
			12.1	45	2.28	12	0.058	0.027
			18.4	26	2.90	12	0.055	0.029
II	3660	26	10.2	28	3.66	6	0.055	0.024
			10.7	40	3.54	18	0.054	0.032
			11.9	13	3.77	18	0.065	0.033
			12.1	0	3.94	18	0.056	0.030
			13.4	17	4.28	6	0.062	0.035
			14.0	0	4.51	6	0.059	0.029
		85	12.3	25	3.93	5	0.064	0.073
			14.1	28	3.79	5	0.066	0.087
		125	15.5	27	3.99	5	0.066	0.102
			16.3	33	3.90	6	0.066	0.088
M	3270	26	10.9	10	0.087	96	0.034	0.111
			11.5	25	0.105	96	0.034	0.112
			12.2	21	0.090	96	0.040	0.129
			16.4	20	0.106	96	0.039	0.137
	3660		12.1	28	0.474	48	0.055	0.031
			14.3	21	0.454	48	0.051	0.026
	3910		11.5	11	0.374	63	0.050	0.010
			13.9	26	0.445	63	0.051	0.014
			15.1	21	0.439	66	0.056	0.016
			15.1	21	0.472	69	0.054	0.013

[a] I, filter combination I; II, filter combination II; M, monochromator.

Table II. Summary of Average Product Quantum Yields and Average Primary Dissociative Yields in Photolysis of Isopropyl Nitrite

Wavelength isolation[a]	λ, Å	Temp, °C	$\Phi_{CH_3COCH_3}$	Φ_{CH_3CHO}	ϕ_1[b]
I	3660	26	0.060	0.028	0.36
II	3660	26	0.059	0.031	0.35
		85	0.065	0.080	0.44
		125	0.066	0.095	0.46
M	3270	26	0.037	0.122	0.33
	3660	26	0.053	0.029	0.32
	3910	26	0.053	0.013	0.31

[a] I, filter I; II, filter II; M, monochromator. [b] The standard error of each mean was 0.01.

the accepted value is 1.0.[7] The light beam was monitored during an illumination with a phototube and pen recorder. The mixture of unchanged nitrite with products condensed at −160° was analyzed by gas chromatography on a 12 ft × 0.25 in. column of 20% tricresyl phosphate on Chromosorb W.

Results

Illumination of isopropyl nitrite vapor in the presence of nitric oxide gave acetone and acetaldehyde as major products, with small amounts of methyl nitrite, methyl nitrate, nitrogen, nitrous oxide, and water. Isopropyl alcohol was usually found, but this was apparently formed by reaction of the nitrite on the gas chromatographic column.[8,9] Search of the volatile part of the reaction mixture with gas chromatography and mass spectrometry revealed no other products. Table I shows quantum yields of acetone and acetaldehyde under various conditions. Table II shows average yields. The main results are (1) the quantum yields are low, but independent of pressure of nitrite and nitric oxide, at least at 26°; (2) as the temperature is increased, the yield of acetone increases slightly and the yield of acetaldehyde increases markedly; (3) in the experiments with the monochromator, the acetaldehyde yield increases as the wavelength is decreased; the acetone yield decreases, at least as the wavelength is changed from 3660 to 3270 Å.

Discussion

The following reactions must be considered

$$(CH_3)_2CHONO + h\nu \longrightarrow \alpha(CH_3)_2CHO^* + [1-\alpha](CH_3)_2CHO + NO \quad (1)$$

$$\longrightarrow CH_3COCH_3 + HNO \text{ (or NOH)} \quad (2)$$

$$(CH_3)_2CHO^* \longrightarrow CH_3CHO + CH_3 \quad (3)$$

$$CH_3 + NO \longrightarrow \text{products} \quad (4)$$

$$(CH_3)_2CHO + NO \longrightarrow CH_3COCH_3 + HNO \quad (5)$$

$$\longrightarrow (CH_3)_2CHONO \quad (6)$$

Primary process 1 has been invoked in several reports on photolysis of alkyl nitrites.[8,10,11] A part of the alkoxy radicals (*) are supposedly vibrationally excited and decompose rapidly by process 3. The acetone quantum yields, Tables I and II, place the primary yield $\phi_2 \leq 0.06$ at 26°. The inequality holds if ϕ_1 is not zero. The available data on photolysis of isopropyl and other nitrites indicate that alkoxy radicals

(7) C. V. Cannon and O. K. Rice, *J. Amer. Chem. Soc.*, **63**, 2900 (1941); ref 1, p 463.
(8) G. R. McMillan, *J. Amer. Chem. Soc.*, **84**, 4007 (1962).
(9) B. E. Ludwig and G. R. McMillan, *J. Phys. Chem.*, **71**, 762 (1967).
(10) G. R. McMillan, J. G. Calvert, and S. S. Thomas, *ibid.*, **68**, 116 (1964).
(11) D. Durant and G. R. McMillan, *ibid.*, 70, 2709 (1966).

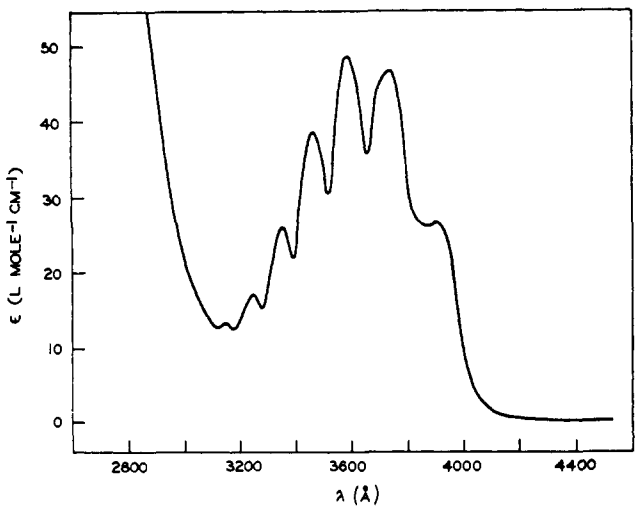

Figure 1. Ultraviolet absorption spectrum of isopropyl nitrite vapor.

are indeed formed in the primary photochemical act, so ϕ_2 is probably much less than 0.06. We are familiar with no experiments which point to the occurrence of process 2. Nitrites are commonly photolyzed under conditions such that disproportionation between the alkoxy radical and nitric oxide is not excluded. These disproportions have been independently established in several systems. We assume ϕ_2 is zero.

From the constancy of the acetone yield under various conditions, it is concluded that steps 5 and 6 are the only fates of the unexcited isopropoxy radical. With $k_6 \sim 10^{10}$ ml mole^{-1} sec^{-1} and k_5 not much smaller,[12] no second-order process can compete with reaction of isopropoxy with nitric oxide. There is available a wide selection of values for k_5/k_6 obtained from photolysis and pyrolysis of diisopropyl peroxide–nitric oxide mixtures. These values,[9,12–14] independent of temperature, include 0.15, 0.17, 0.17, and 0.22. We currently interpret our pyrolysis data[9] to give not 0.17 but 0.21 for k_5/k_6. For this reason, the value of 0.22 published by Hughes and Phillips[13] is adopted in this paper. It is thus assumed that the unexcited isopropoxy radicals formed in step 1 are truly unexcited so that k_5/k_6 obtained from studies of the thermally equilibrated radicals in the pyrolysis is appropriate. This assumption is supported by two considerations. (1) Two-thirds of the isopropoxy radicals formed in photolysis of diisopropyl peroxide vapor at 2537 Å are excited, but the k_5/k_6 describing the unexcited fraction[14] is about 0.17, which is in the range of values determined in pyrolysis experiments. (2) There is apparently a bimodal energy distribution among *t*-pentoxy radicals formed in photolysis of *t*-pentyl nitrite; that is, the radicals are either excited or truly unexcited.[11]

If $k_5/k_6 = 0.22$ is accepted, the mechanism gives the following expression for the primary dissociative yield.

$$\phi_1 = \Phi_{CH_3CHO} + 5.55\Phi_{CH_3COCH_3}$$

(12) M. J. Yee Quee and J. C. J. Thynne, *Trans. Faraday Soc.*, **64**, 1296 (1968).
(13) G. A. Hughes and L. Phillips, *J. Chem. Soc.*, *A*, 894 (1967).
(14) G. R. McMillan, *J. Amer. Chem. Soc.*, **83**, 3018 (1961).

The primary yield was calculated for each experiment in Table I. Average values under given conditions are presented in Table II. It should be emphasized that the calculation of ϕ_1 depends critically on k_5/k_6, so the values of ϕ_1 must be accepted only with reservations. Even though the several studies give values of k_5/k_6 in fair agreement, the mechanisms of reactions leading to these values are far from completely understood. The primary quantum yield is seen to be considerably less than unity, in contrast to the *t*-butyl compound under similar conditions.[3] The primary yield increases slightly with temperature and is independent of wavelength. The yield is the same with each of the filter systems used to isolate 3660-Å light, but these values are slightly higher than in the 3660-Å experiments with the monochromator.

Light absorption in the long-wavelength (n,π*) band system of alkyl nitrites (Figure 1) is perhaps best understood from the very similar spectrum of nitrous acid.[15] The simple progression arises from excitation of the terminal N=O stretching mode in the upper state; the (0–0) band is prominent. The entire system appears diffuse under highest resolution.

The (n,π*) state is not RO–NO antibonding. Presumably decomposition occurs through the (n,σ*) state associated with the continuum (λ_{max} ~2200 Å).[16] If so, the ^{3}(n,σ*) level is placed $\leq$73 kcal above the ground by observation of efficient photodecomposition at 3910 Å, in the (0–0) band of the ^{1}(n,π*) transition. Direct excitation into the ^{1}(n,σ*) system leads to process 1 with a primary yield $\geq$0.86 and probably unity.[17]

Excitation of the ^{1}(n,π*) state with 1–2 or 4–6 quanta in the terminal N=O stretching vibration leads to no more efficient decomposition than does excitation of the vibrationless state. This is not because of vibrational relaxation before decomposition. Table II shows that although the primary yield is independent of wavelength, the product distribution, which reflects the relative importance of excited and unexcited radicals, is significantly wavelength dependent. It is found here, as in other cases,[8,11,14] that more excited alkoxy radicals are formed at shorter wavelengths.

Formal excited state schemes can be constructed based on the temperature and wavelength dependence of the over-all and primary yields. There may be an initial partition between two paths, one leading to the (n,σ*) state and decomposition; the other, to inevitable deactivation.[18] This initial partition, slightly dependent on temperature but unaffected by vibrational excitation in the N=O stretching mode, determines the

(15) G. W. King and D. Moule, *Can. J. Chem.*, 40, 2057 (1962).
(16) R. C. Mitchell and J. P. Simons, *Discussions Faraday Soc.*, **44**, 208 (1967).
(17) Reference 1, p 483. This work was carried out at Celanese Chemical Co. in 1962. When isopropyl nitrite was photolyzed at 2537 Å in the presence of nitric oxide, the acetaldehyde quantum yield was 0.86. This represents the yield of excited isopropoxy radicals so is a lower limit for the quantum yield of isopropoxy formation.
(18) Possibly through the "thermal isomer" suggested by Napier and Norrish[19] to account for eventual re-formation of methyl nitrite following flash excitation. The pressure independence of the primary yield found in the present study, together with decomposition observed in solution, indicates that deactivation does not compete with decomposition.
(19) I. M. Napier and R. G. W. Norrish, *Proc. Roy. Soc.*, **A299**, 317 (1967).

primary quantum yield for decomposition. A second partition, dependent on both wavelength and temperature, determines the fraction of excited radicals formed. We cannot at present offer a less diffuse rationalization.

Possible differences in the photochemistry of the *cis* and *trans* forms of nitrites have been considered.[20] The tentative conclusion from the present work is that the primary dissociative yield is the same for both rotamers in the banded region. Isopropyl nitrite is 76% *trans* at 25° in the gas phase.[21] The extinction coefficients of the two forms are not known, but Tarte concluded from examination of band contours that $\epsilon_{trans} < \epsilon_{cis}$ for a given band.[22] It is unlikely that the two forms absorb the same relative fractions of light at the three different wavelengths. Since the observed primary yield is the same at the three wavelengths (Table II), probably the primary dissociative yields of the two forms are the same.

Acknowledgment. We are grateful for support of this work through a research grant from the National Air Pollution Control Administration, Consumer Protection and Environmental Health Service, Public Health Service.

(20) H. W. Brown and G. C. Pimentel, *J. Chem. Phys.*, **29**, 883 (1958); ref 1, p 481.
(21) P. Gray and M. J. Pearson, *Trans. Faraday Soc.*, **59**, 347 (1963).
(22) P. Tarte, *J. Chem. Phys.*, **20**, 1570 (1952).

Electron–Nuclear Double Resonance in Solutions. II. Substituent Effects in Triphenylmethyl Radicals

Robert D. Allendoerfer and August H. Maki[1]

Contribution from the Department of Chemistry, University of California, Riverside, California 92502. *Received September 30, 1968*

Abstract: The electron–nuclear double resonance (ENDOR) spectra of a series of six methyl- and fluorine-substituted triphenylmethyl radicals have been observed and measured. ENDOR of the protons was observed at −70° in toluene solution. No fluorine ENDOR was detected in the fluorinated radicals, and possible reasons for the lack of signals are advanced. Fluorine coupling constants were assigned from the electron spin resonance spectra. Fluorine and methyl substitution in *meta* and *para* positions is found to have little effect on the spin density distribution, whereas the large effect of *ortho* substitution is consistent with a sterically induced twisting of the substituted ring from the plane of the four central carbon atoms. Deviations of *ortho*-methyl proton and fluorine coupling constants from the values expected on the basis of a simple π-electron model is ascribed to a direct interaction between orbitals of the substituent and the π orbital of the central carbon atom which contains a large positive spin density.

The effect of substituents on the properties of triarylmethyl radicals and carbonium ions has long been a subject of considerable interest to organic and theoretical chemists. Substituents affect the stability of the carbonium ions in sulfuric acid[2] and their optical absorption spectra.[3] The dissociation constants of the various hexaarylethenes and the stability of the corresponding triarylmethyl radicals are also affected.[4,5] Attempts to justify this behavior through valence bond and molecular orbital theory have been frustrated largely by lack of knowledge of the conformation of the phenyl rings about the central carbon atom.[6,7] It seems clear from electron spin resonance (esr) and nuclear magnetic resonance (nmr) data that the rings of the triphenylmethyl radical and its carbonium ion are equivalent in solution. Thus, as in the crystal,[8] the rings are probably twisted by the same amount into a propeller conformation with the three carbon–phenyl bonds forming a plane. When a ring substituent is added to the carbonium ion, Kurland, *et al.*,[9] have shown from nmr studies that the rings are no longer magnetically equivalent. Until recently, esr spectra of many of the substituted triarylmethyl radicals have been too complex to interpret, but electron–nuclear double resonance (ENDOR) studies of these systems has led to straightforward interpretation of the proton hyperfine splittings.[10–12]

In this communication, we report on the results of ENDOR and esr measurements on a series of methyl- and fluorine-substituted triphenylmethyl radicals. Cor-

(1) Author to whom correspondence should be addressed.
(2) M. S. Newman and N. C. Deno, *J. Am. Chem. Soc.*, **73**, 3644 (1951).
(3) G. N. Lewis, T. T. Magel, and D. Lipkin, *ibid.*, **64**, 1774 (1942).
(4) C. S. Marvel, J. F. Kaplan, and C. M. Himel, *ibid.*, **63**, 1892 (1941).
(5) S. T. Bowden and D. L. Clarke, *J. Chem. Soc.*, 883 (1940).
(6) M. Szwarc, *Discussions Faraday Soc.*, **2**, 39 (1947).
(7) C. A. Coulson, *ibid.*, **2**, 9 (1947).
(8) A. H. Gomes de Mesquita, C. H. MacGillavry, and K. Eriks, *Acta Cryst.*, **18**, 437 (1965).
(9) R. J. Kurland, I. I. Schuster, and A. K. Colter, *J. Am. Chem. Soc.*, **87**, 2278, 2279 (1965).
(10) J. S. Hyde, *J. Chem. Phys.*, **43**, 1806 (1965).
(11) J. S. Hyde, R. Breslow, and C. DeBoer, *J. Am. Chem. Soc.*, **88**, 4763 (1966).
(12) A. H. Maki, R. D. Allendoerfer, J. C. Danner, and R. T. Keys, *ibid.*, **90**, 4225 (1968).