

The Kinetics of Photochemical Reactions. Part IV.¹ Photoreduction of Carbonyl Triplets by Bonds other than C-H. Semiempirical Calculations

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A modified B.E.B.O. (Bond Energy–Bond Order) method has been used to calculate kinetic parameters for the reactions of carbonyl triplets with various substrates having X–H bonds (where X is not carbon). The results are compared with experiment where this is possible. The possibility of abstraction of hydrogen atoms bonded to oxygen or nitrogen should be taken into account rather than disregarded *a priori*.

UNTIL a decade ago the study of free-radical abstraction reactions was virtually limited to the cleavage of C–H bonds and in exceptional cases to halogen–hydrogen bonds. Photochemical radical-like processes are among the most common reactions of excited species; in particular, the photoreduction of carbonyl compounds is a well known process. However, nearly all the quantitative studies refer to the cleavage of C–H bonds, with a few exceptions involving the cleavage of other X–H bonds or an S_H2 attack at metallic centres.² The field of photoreductions involving the cleavage of bonds other than C–H is as important as it is unexplored.

The photoreduction of carbonyl compounds can occur either by a radical-like or a charge-transfer mechanism. It has been pointed out that these two possibilities correspond to the extremes of a continuum involving variable degrees of both types of interactions.² The semiempirical model which we use in this work corresponds to a 'pure' radical-like mechanism. The availability of an estimated rate constant for the radical-like process can also be helpful when deciding between this and the charge-transfer mechanism.³ This point is further developed later.

In previous parts we have been concerned with the application of a modified Bond Energy–Bond Order (B.E.B.O.) method to reaction (1),⁴ where $R^1R^2CO^*$ is a thermalized n,π^* triplet state. Most of the examples



considered in previous publications involved carbon centred $X\cdot$ radicals.^{4b} In this paper we examine systematically the possibility of using the same method for systems where the bond cleaved is other than C–H.

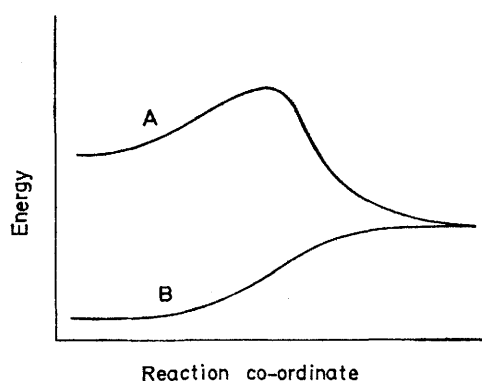
According to Dougherty's classification⁵ this reaction can be regarded as an N type process. The potential energy profile for these reactions is qualitatively shown in the Figure. The application of the modified B.E.B.O. method is equivalent to the assumption of a particular

¹ Part III, J. Grotewold, D. Soria, C. M. Previtali, and J. C. Scaiano, *J. Photochem.*, 1972–1973, **1**, 471.

² J. C. Scaiano, *J. Photochem.*, 1973–1974, **2**, 81.

shape for curve A in the Figure. Curve B (right to left) corresponds to the back disproportionation of the radicals to yield X–H and a ground state carbonyl molecule.

In this method the carbonyl oxygen is responsible for most of the interaction with the hydrogen donor. In those systems where the observed process is other than radical-like hydrogen abstraction (*e.g.* charge-transfer or



Potential energy profiles: A for reaction (1); B (right to left) for the disproportionation of the radicals produced in reaction (1)

quenching, following or not exciplex formation) one would expect the method to underestimate the rate constant. In other words, for a process to compete favourably with radical-like abstraction it must be faster than this. However, one must keep in mind that the method can be used to estimate rate parameters *given* the mechanism, but not to predict a mechanism, unless a similar calculation could be performed for other possible reaction paths.

RESULTS

The calculations were carried out using the semiempirical B.E.B.O. method, modified in order to take into account

³ S. G. Cohen, A. Parola, and G. H. Parsons, jun., *Chem. Rev.*, 1973, **73**, 141.

⁴ C. M. Previtali and J. C. Scaiano, *J.C.S. Perkin II*, (a) 1972, 1667; (b) p. 1672.

⁵ R. C. Dougherty, *J. Amer. Chem. Soc.*, 1971, **93**, 7187.

specific interactions of the excited state. The details and mode of application of the method have been reported elsewhere.⁴

Theoretical rate constants were obtained from equation (2) where V^* is the potential energy at the maximum of the

$$k = B \exp(-V^*/RT) \quad (2)$$

energy profile obtained using equation (3), where all the

$$V = E_1 - E_1 m^p - E_2 m^q - (E_t - E_d)m + V_{\text{rep}} + V_{\text{rep}'} \quad (3)$$

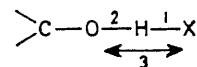
symbols have their usual meaning.^{4a,6} $V_{\text{rep}'}$ was roughly estimated as 10% of V_{rep} as proposed previously.^{4a} B is the theoretical pre-exponential factor obtained from equation (4) where B' is obtained classically from the structural

$$B = B' B_o B_\Gamma \quad (4)$$

parameters of the activated complex [the curvature of equation (3) at the maximum and the bond lengths], B_o is the chemical degeneracy (*i.e.* the number of equivalent reactive

experimental frequencies (see SUP 21348). This repulsive term and associated bond parameters correspond to the single bonded diatomic molecule between terminal atoms (ground state), which in many cases does not exist. When this is the case an estimation must be made from related bond properties in polyatomic molecules (*e.g.* >C-O- in ethers or alcohols as an approximation to the C-O single bonded molecule).

The structural parameters for the carbonyl compounds were the same as in Part I.^{4a} The corresponding parameters for the hydrogen donor and for the calculation of the repulsive potential (V_{rep}) have been included in SUP 21348. The subscripts used in the Tables correspond to model (A).



(A)

In order to calculate B' it was necessary to know the stretching force constants corresponding to the diatomic molecules 1, 2, and 3. Many of these were not available in

TABLE I
Calculated kinetic parameters for $(E_t - E_d) = 18.4 \text{ kJ mol}^{-1 a}$

Substrate	ΔH^a	n^*	V^*^a	$-F_p^b$	ν^*^c	E^a	$\log k^d$
PH ₃	-75.7	0.92	5.52	0.087	128	8.15	8.12
Me ₃ GeH	-148.0	0.96 _s	4.31	0.062	93	7.90	8.14
GeH ₄	-88.6	0.92	7.65	0.110	131	10.62	7.66
R ₂ NH	-68.6	0.82	16.43	0.227	286	15.59	5.95
RNH ₂	-47.7	0.73	21.74	0.323	425	16.97	5.71
NH ₃	-22.6	0.60	31.14	0.452	854	21.86	4.86
N ₂ H ₄	-135.4	0.94	8.19	0.102	159	11.20	8.00
ROH	-18.4	0.63	19.06	0.334	618	8.82	6.75
H ₂ O	-31.8	0.30	49.16	0.328	460	41.47	1.05
H ₂ O ₂	-79.0	0.91	5.18	0.089	150	6.86	8.31
C ₆ H ₅ OH	-85.3	0.93	4.56	0.072	131	7.06	8.17
SiH ₄	-60.2	0.83	13.38	0.201	229	14.09	6.63
Me ₃ SiH	-114.5	0.94	6.98	0.092	131	10.16	7.43
FH	+115.4	0.06 _s	119.84	0.080	132	120.38 ^e	< -9
ClH	-22.2	0.78	20.69	0.211	256	19.06	5.00
BrH	-90.7	0.98 ₂	1.46	0.022	53	5.31	9.31
IH	-155.1	0.99 _s	0.17	0.003	18	4.31	10.91
H ₂	-17.6	0.59	23.12	0.408	1022	13.88	6.45
SH ₂	-68.6	0.84	21.69	0.250	247	23.07	4.71
MeSH	-85.3	0.87	19.14	0.222	220	20.82	4.91
SnH ₄	-106.2	0.94	7.32	0.095	114	10.74	7.83
R ₃ SnH	-139.6	0.96 _s	5.85	0.072	97	9.49	7.78

^a In kJ mol⁻¹. ^b In mdyn Å⁻¹. ^c In cm⁻¹. ^d k in l mol⁻¹ s⁻¹ at 298 K. ^e The value reflects the high enthalpy change.

hydrogen atoms), and B_Γ is the quantum correction term, including a tunnelling correction. B is related to the experimental A factor by equation (5) where θ is the temperature coefficient given by equation (6).

$$A = B \exp \theta \quad (5)$$

$$\theta = \partial (\ln B) / \partial (\ln T) \quad (6)$$

A summary of the bond properties used as input data is given in Supplementary Publication No. SUP 21348 (4 pp.).[†] Large discrepancies in the published data are unfortunately quite common and in many cases the choice of 'best' parameters is difficult and might be regarded as speculative. Bond dissociation energies (D°_{298}) for the bonds being broken and formed were used without zero point energy corrections; therefore E_1 and E_2 in equation (3) were replaced by D°_{298} . The correction was taken into account in the calculation of non-bonded atom repulsions; it was evaluated from the

[†] For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue. Items less than 10 pp. are supplied as full-size copies.

the literature and had to be estimated from the observed frequencies using a diatomic harmonic oscillator equation (7)

$$\nu = (1/2\pi)(F/\mu)^{1/2} \quad (7)$$

where F is the force constant, μ the reduced mass, and ν the experimental frequency.

The Morse parameter (β) used for the calculation of the repulsive term was evaluated from experimental data from equation (8) where ν_{str} is given in cm⁻¹, μ in atomic units,

$$\beta = 1.2177 \times 10^7 \nu_{\text{str}} (\mu/349.76D)^{1/2} \quad (8)$$

D in kcal mol⁻¹, and β in Å⁻¹. In the calculation of the pre-exponential factor a four-particle correction was introduced in the same way as previously discussed.⁷ B' in equation (4) already contains this correction.

The results of the calculations are shown in Tables 1-3.

⁶ H. S. Johnston, 'Gas Phase Reaction Rate Theory,' Ronald Press, New York, 1966.

⁷ C. M. Previtali and J. C. Scaiano, *J. Chem. Soc. (B)*, 1971, 2317.

The kinetic parameters, as well as the main structural parameters of the activated complex have been included. n^* is the bond order of the bond being cleaved (X-H), F_p the reaction co-ordinate force constant at the maximum (*i.e.* the curvature of the energy profile), and ν^* the corresponding imaginary vibration frequency. The Arrhenius activation

results obtained taking into account the complete energy surface.⁶ (ii) Since ν^* is generally small (see Tables 1—3), the correction, in most cases would not exceed 20% of the rates given in the Tables.⁶ The only exceptions for which the tunnelling correction could be considerably larger are H_2 and NH_3 (see the values of ν^* in Tables 1—3).

TABLE 2
Calculated kinetic parameters for $(E_t - E_d) = -4.18 \text{ kJ mol}^{-1}$ ^a

Substrate	ΔH	n^*	V^*	$-F_p$	ν^*	E	$\log k$
PH ₃	-53.1	0.86	7.98	0.137	177	9.28	7.52
Me ₃ GeH	-125.4	0.955	5.18	0.073	102	8.65	7.81
GeH ₄	-66.0	0.88	9.91	0.147	160	12.08	7.12
R ₂ NH	-46.0	0.74	22.15	0.306	402	17.14	5.41
RNH ₂	-25.1	0.63	28.93	0.412	703	20.23	4.99
NH ₃	0.0	0.49	41.38	0.494	1309	31.56	3.06
N ₂ H ₄	-112.9	0.92	9.74	0.123	178	12.25	7.63
ROH	4.2	0.47	29.22	0.372	1080	17.51	5.11
H ₂ O	54.3	0.20	66.09	0.221	288	63.24	-2.77
H ₂ O ₂	-56.4	0.85	7.73	0.140	205	7.40	7.85
C ₆ H ₅ OH	-62.7	0.88	6.73	0.113	176	7.57	7.70
SiH ₄	-37.6	0.74	18.10	0.281	337	16.18	6.01
Me ₃ SiH	-92.0	0.91	8.67	0.119	157	11.24	6.95
FH	137.9	0.04 ₅	141.20	†	†	†	†
ClH	0.4	0.65	27.04	0.223	456	20.65	4.38
BrH	-68.1	0.97 ₂	1.96	0.029	63	5.64	9.04
IH	-132.5	0.99 ₇	0.21	0.004	21	4.35	10.75
H ₂	5.0	0.46	33.86	0.453	1349	23.62	4.61
SH ₂	-46.0	0.78	26.00	0.298	307	25.33	4.12
MeSH	-62.7	0.83	22.53	0.261	255	23.07	4.35
SnH ₄	-83.6	0.93	8.69	0.109	125	11.91	7.46
R ₃ SnH	-117.0	0.95 ₅	6.77	0.084	106	10.32	7.44

^a Units as in Table 2. † Values reflect the high enthalpy change.

TABLE 3
Calculated kinetic parameters for $(E_t - E_d) = -24.7 \text{ kJ mol}^{-1}$ ^a

Substrate	ΔH	n^*	V^*	$-F_p$	ν^*	E	$\log k$
PH ₃	-32.6	0.78	11.58	0.198	252	10.70	6.97
Me ₃ GeH	-104.9	0.94	6.27	0.089	115	9.53	7.46
GeH ₄	-45.6	0.82	12.92	0.197	208	13.71	6.57
R ₂ NH	-25.5	0.64	27.80	0.391	654	19.40	4.84
RNH ₂	-4.6	0.52	37.62	0.458	1243	27.84	3.57
NH ₃	+20.5	0.38	52.92	0.458	786	44.18	2.22
N ₂ H ₄	-92.4	0.89	11.70	0.152	208	13.25	7.23
ROH	+24.7	0.33	41.47	0.302	495	32.81	2.27
H ₂ O	+74.8	0.14	83.14	0.160	216	82.85	-6.16
H ₂ O ₂	-35.9	0.77	11.54	0.203	294	8.03	7.46
C ₆ H ₅ OH	-42.2	0.80	9.99	0.177	256	7.61	7.34
SiH ₄	-17.1	0.63	24.41	0.350	593	20.48	5.14
Me ₃ SiH	-71.5	0.88	10.78	0.149	181	12.75	6.50
FH	+158.4	0.03 ₀	160.97	†	†	†	†
ClH	+20.9	0.44	36.16	0.118	489	28.72	2.89
BrH	-47.7	0.95 ₅	2.72	0.041	76	6.02	8.55
IH	-112.0	0.99 ₅	0.27	0.004	24	4.39	10.64
H ₂	+25.5	0.34	46.23	0.383	1282	37.12	2.26
SH ₂	-25.5	0.71	31.22	0.337	404	27.96	3.50
MeSH	-42.2	0.77	26.67	0.303	318	25.21	3.79
SnH ₄	-63.1	0.90	10.45	0.137	145	13.17	6.99
R ₃ SnH	-96.6	0.94	7.90	0.100	117	11.24	7.09

^a Units as in Table 2. † Values reflect the high enthalpy change.

energy was obtained from the classical value from equation (9) where θ includes all the quantum effects, except tunnelling, and is obtained using equation (6). We note that the

$$E = V^* + \theta RT \quad (9)$$

'activation energy' reported in previous papers corresponds to V^* .^{1,4,8} Tunnelling effects were not taken into account for two reasons. (i) The only tunnelling correction which can be easily introduced into the B.E.B.O. method approximates the potential energy profile by a one dimensional Eckart barrier, and this differs considerably from the

DISCUSSION

Kinetics studies involving systems where the bond cleaved is not C-H have not been frequent. Table 4 shows a comparison of experimental and calculated parameters. We note that while the experimental rate constants correspond to the 'molecular reaction', the calculated values correspond to reaction exclusively at the site indicated in SUP 21348; *e.g.* in Bu₃SnH, only

⁸ C. M. Previtali and J. C. Scaiano, *J. Photochem.*, 1973—1974, **2**, 321.

to the Sn-H bond. Moreover, it should be kept in mind that the calculated parameters correspond to the gas phase. We have already pointed out previously⁴ that the agreement is reasonably good when the comparison is carried out with parameters obtained in non-polar solvents and the calculated activation energy exceeds the formal value for diffusion (usually between 8 and 16 kJ mol⁻¹).^{4,9}

The results of the calculations in the case of O-H bonds are particularly interesting. Several of the rate constants obtained are well into the expected observable range. We could not find any evidence as to whether the reaction can take place or not in the case of alcohols, one of the most widely studied examples of photoreduction.² Alkoxy radicals, one of the products of these reactions, are not usually observable by e.s.r. spectroscopy; moreover, the reaction which alkoxy radicals are most likely to undergo is hydrogen abstraction from the solvent or substrate. The reasons given above, together with the fact that the rate of production of alkoxy radicals will

excited carbonyl compounds is proposed have been published. In the biacetyl-phenol system, Turro and Engel¹³ have proposed that reversible abstraction of the phenolic hydrogen takes place. Ledger and Porter¹⁴ have observed the formation of ketyl radicals in the irradiation of benzophenone in pure water (see Table 4). The rate constant for this process is considerably larger than our calculated value; however, for endothermic reactions our method is extremely sensitive to the uncertainties in the bond dissociation energies and in this particular case the enthalpy change estimated by us is considerably different from that proposed by Ledger and Porter.¹⁴ In addition, the B.E.B.O. method does not take into account polar effects in reactants, and when such effects are important, serious discrepancies between calculated and experimental rate constants have been observed.¹⁵ Hydrogen bonding could also be of importance.

In the case of halogen-hydrogen bonds the calculated parameters suggest that abstraction should be observable

TABLE 4
Comparison of experimental and calculated parameters for some monoketones

Carbonyl compound	Substrate	Medium	Temp. (°C)	log <i>k</i> (exp) ^a	log <i>k</i> (calc) ^a	Ref.
Me ₂ CO	SiH ₄	Gas	25	6.30	6.63	24
Me ₂ CO	BrH	Gas	25	8.78	9.31	<i>b</i>
Me ₂ CO	Bu ₃ SnH	n-Hexane	r.t. ^c	8.30	7.78	<i>d</i>
Me ₂ CO	Et ₂ N	Gas	100	7.40	6.52 ^e	20
Me ₂ CO	Me ₂ N	Gas	100	7.40	6.52 ^e	20
Et ₂ CO	Et ₂ N	Gas	30	7.72	6.02 ^e	20
Ph ₂ CO	H ₂ O	Neat	r.t. ^c	0.70	-6.16 ^f	14
Ph ₂ CO	Bu ₃ SnH	Benzene	r.t. ^c	7.67	7.09	<i>g</i>

^a *k* in l mol⁻¹ s⁻¹. ^b C. W. Larson and H. E. O'Neal, *J. Phys. Chem.*, 1966, **70**, 2475. ^c Room temperature. ^d See refs. 4*b* and 25.

^e Since experimental rate constants involve abstraction from C-H and N-H bonds, they are an upper limit for the reactivity of N-H bonds. The discrepancies in input parameters for N-H bonds lead to considerable uncertainties in the calculations (see text).

^f See text for discussion. ^g D. R. G. Brimage, R. S. Davidson, and P. F. Lambeth, *J. Chem. Soc. (C)*, 1971, 1241.

always be smaller than the corresponding rate for ketyl radicals (because at least one ketyl radical always results from the ketone group), and the lifetime of the former will be shorter led us to the conclusion that the formation of alkoxy radicals could easily have remained unobserved. At least, it seems certain that the frequent assumption that the site of reaction of carbonyl triplets with alcohols is *always* a C-H bond lacks theoretical and experimental support. Further, a similar assumption has been made frequently in the case of alkoxy radicals (frequently considered good analogues of carbonyl triplets).^{2,10} This assumption has recently been shown to be incorrect. Griller and Ingold¹¹ have shown that alkoxy radicals abstract hydrogen atoms from O-H bonds at a rate comparable to the rate of abstraction from a primary C-H bond. Methyl and phenyl radicals also react with methanol abstracting hydrogen atoms bonded to oxygen, as well as those directly bonded to carbon.¹² A few examples where a similar reaction by

⁹ J. C. Scaiano, J. Grotewold, and C. M. Previtali, *J.C.S. Chem. Comm.*, 1972, 390.

¹⁰ C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, 1965, **87**, 3361.

¹¹ D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, 1974, **96**, 630.

¹² E. Ratajczak and A. F. Trotman-Dickenson, 'Supplementary Tables of Bimolecular Gas Reactions,' O.S.T.I., Cardiff, 1969.

for all the ketones considered to react with hydrogen bromide and hydrogen iodide and probably in the case of hydrogen chloride in some cases. Quantitatively the only possible comparison is for the acetone-HBr system where the calculated values agree well with the experimental parameters (see Table 4 and ref. 4*a*).

Amines, together with ammonia and hydrazine, constitute another series of interesting examples. The calculated rates are high enough to be observable in the absence of competing bimolecular processes. This condition might be fulfilled in the case of hydrazine or amines having weak N-H bonds and rather strong C-H bonds in the gas phase, where charge transfer is unlikely to occur. We note that our calculations in the case of amines might be vitiated by errors in the bond dissociation energies; the values reported show large discrepancies. For example Kerr¹⁶ reports a value of 359.5 for Me₂NH and 430.5 kJ mol⁻¹ for NH₃, while Benson *et. al.*¹⁷ report values of 397.1 and 459.8 kJ mol⁻¹ respectively. Recent

¹³ N. J. Turro and R. Engel, *J. Amer. Chem. Soc.*, 1969, **91**, 7113.

¹⁴ M. B. Ledger and G. Porter, *J.C.S. Faraday I*, 1972, 539.

¹⁵ N. L. Arthur and J. A. McDonnell, *J. Chem. Phys.*, 1972, **56**, 3100.

¹⁶ J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465.

¹⁷ D. M. Golden, R. K. Solly, N. A. Gac, and S. W. Benson, *J. Amer. Chem. Soc.*, 1972, **94**, 363.

reports¹⁸ give a value of $D_0^0(\text{NH}_2\text{-H})$ of 443.1 kJ mol⁻¹. Zavitzas¹⁹ propose values of 438.9 and 405.5 kJ mol⁻¹ for ammonia and methylamine respectively. We have chosen values which maintain reasonable differences in bond dissociation energies which reflect the lability of the N-H bonds in the different molecules. Recent experiments using alkanone-dialkylamine systems in the gas phase suggest that N-H cleavage competes with C-H cleavage.²⁰

Phosphorus-hydrogen bonds can be expected to be highly reactive; however, it would be hardly surprising if the process is other than hydrogen abstraction, since other phosphorus compounds (*e.g.* Ph₃P) have been shown to be excellent quenchers of carbonyl triplets.²¹

Zepp and Wagner²² have studied the acetophenone-butanethiol system in benzene and found that the quenching of the ketone triplets takes place with a rate constant of 1.4×10^7 l mol⁻¹ s⁻¹. From the isotopic dependence of the slopes of the Stern-Volmer plots the authors conclude that hydrogen abstraction is not the main route for triplet removal from the system. Consistently with this observation, the calculated rate constant is considerably lower than the experimental value (see Table 4).

In the case of silicon-hydrogen bonds, these have been shown to be reactive in solution²³ and in the gas phase.²⁴ In the latter, O'Neal *et al.* have carried out kinetic measurements for the acetone-silane system.

¹⁸ D. K. Dohme, R. G. Hemsworth, and H. W. Rundle, *J. Chem. Phys.*, 1973, **59**, 77.

¹⁹ A. A. Zavitzas, *J. Amer. Chem. Soc.*, 1972, **94**, 2779.

²⁰ E. B. Abuin, M. V. Encina, E. A. Lissi, and J. C. Scaiano, *J.C.S. Faraday I*, in the press.

Tin-hydrogen bonds are known to be quite reactive,² and the reaction has frequently been used as a test for triplet reactivity.²⁵ The calculated rate constants compare well with the experimental parameters. We could not find any report in the literature referring to germanium-hydrogen bonds. Considering the reactivity of silicon- and tin-hydrogen bonds it seems reasonable to assume that germanium-hydrogen bonds will also be reactive.

Finally, we conclude that (i) our modification of the B.E.B.O. method is a convenient tool for the prediction of X-H bond reactivities towards carbonyl triplets in radical-like reactions; (ii) when the experimental rate constants are considerably higher than the calculated values, this can usually be taken to mean that a mechanism other than a radical-like abstraction is operative (charge-transfer interactions are frequently responsible for this type of behaviour); (iii) further experimental studies are certainly needed for many of the systems considered herein. In particular the cleavage of O-H and N-H bonds obviously deserves critical examination.

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²¹ J. C. Scaiano, *J. Photochem.*, 1973-1974, **2**, 471.

²² R. G. Zepp and P. J. Wagner, *J.C.S. Chem. Comm.*, 1972, 167.

²³ H. D. Becker, *J. Org. Chem.*, 1969, **34**, 2469.

²⁴ H. E. O'Neal, S. Pavlou, T. Lubin, M. A. Morey, and L. Batt, *J. Phys. Chem.*, 1971, **75**, 3945.

²⁵ P. J. Wagner, *J. Amer. Chem. Soc.*, 1967, **89**, 2503, and references therein.