The Kinetics of Photochemical Reactions. Part I. Application of a Modified Bond-Energy–Bond-Order Method to the Atom Abstraction Reactions of Excited Carbonyl Compounds

By **Carlos M. Previtali,** Facultad de Farmacia y Bioquimica, Universidad de Buenos Aires, Junin 956, Buenos Aires, Argentina
Juan C. Scaiano,*† Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ

A modification of the Bond-Energy–Bond-Order method has been applied to the intermolecular photoreduction of carbonyl compounds. It provides a way of predicting the kinetics of these reactions as well as an insight into the role of the different thermodynamic parameters and the shape of the potential energy surface. The results strongly support the biradical model for the carbonyl triplet, in which the oxygen atom is formally considered as a free radical centre. A comparison with alternative models is also carried out.

THE reactivity of photoexcited molecules has been the subject of a very large number of studies during the last few years.[1] It would be highly desirable to carry out a theoretical treatment of some of these processes; however, this is a very difficult problem, as even for the simplest thermal reactions a series of severe simplifying assumptions become necessary. These difficulties led to the development of a series of semiempirical methods, among which Johnston and Parr's Bond-Energy–Bond-Order (B.E.B.O.) method [2] is one of the most successful for the prediction of gas-phase kinetic data. It has been applied to a wide range of reactions including hydrogen abstraction,[3] radical disproportionation,[4] flame reactions,[5] halogen atom transfer,[5,6] and multivalent atom transfer.[7]

The $^3n \longrightarrow \pi^*$ state of carbonyl compounds is known to show radical-like behaviour,[8,9] and in particular, alkoxyl radicals are good analogues.

We have developed a kinetic model based on the B.E.B.O. method [10] which allows the evaluation of potential energy profiles for reaction (1) in the gas-phase. From these profiles the activation energy can

$$R^1R^2CO^* + R^3\text{–}H \longrightarrow R^1R^2\dot{C}OH + R^3\cdot \qquad (1)$$

be obtained, and, by application of a suitable version of transition-state theory the pre-exponential factors can be evaluated.

Kinetic Model.—The assumptions involved in the derivation of the B.E.B.O. method, as well as its application to hydrogen transfer reactions have been widely discussed, and detailed considerations can be found elsewhere.[2,11] For a reaction such as (2), the potential energy along the reaction co-ordinate (that of constant

$$B\cdot + AH \longrightarrow A\cdot + BH \qquad (2)$$

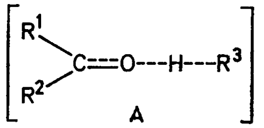
bond-order sum) can be evaluated using equations (3)—(5), where all the symbols have their usual meaning.[10,11]‡

$$V = E_1 - E_1n^p - E_2m^q + V_{\text{rep}} \qquad (3)$$

$$V_{\text{rep}} = \tfrac{1}{2}E_3 \exp(-\beta r_3)\,[1 + \tfrac{1}{2}\exp(-\beta r_3)] \qquad (4)$$

$$r_3 = R_1 + R_2 - R_{3s};\ n + m = 1 \qquad (5)$$

In the carbonyl triplet the electronic excitation energy contributes to decrease the double bond character of the C–O bond, due to the promotion of a *non*-bonding electron to a π^* antibonding orbital. This formally leaves seven electrons around the oxygen atom. The carbonyl group can then be considered as a biradical,[12] with the oxygen atom as a true free radical centre. Therefore, the transition state for reaction (1) can be written as A where the dotted lines indicate fractional bond orders.


A

Another insight into the role of the triplet state energy (E_t) can be obtained by comparison of the expressions for the enthalpy changes of reactions (1) and (6), where E_d is the difference between the dissociation energies of

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† *Present address:* Departamento de Quimica, Universidad Tecnica del Estado, Casilla 4587, Santiago, Chile.

‡ Subscript 1 refers to the bond being broken, 2 to the bond being formed and 3 to the A–B distances or interactions. The relation between bond orders and lengths is given by, *e.g.* $R_2 = R_{2s} - 0{\cdot}6 \log_{10}m$.

[1] See, for example: 'Photochemistry: A Specialist Periodical Report,' ed. D. Bryce-Smith, vols. 1 and 2, The Chemical Society, London, 1970 and 1971.

[2] H. S. Johnston and C. Parr, *J. Amer. Chem. Soc.*, 1963, **85**, 2544.

[3] S. W. Mayer and L. Schieler, *J. Phys. Chem.*, 1968, **72**, 236, and references therein.

[4] R. L. Thommarson, *J. Phys. Chem.*, 1970, **70**, 938; E. Lissi, M. Passeggi and C. Previtali, *Anales Asoc. quim. Argentina*, 1970, **58**, 167.

[5] S. W. Mayer, L. Schleiler, and H. S. Johnston, 'Proceedings of the Eleventh International Symposium on Combustion,' The Combustion Institute, Pittsburg, 1967, p. 387.

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

[7] S. W. Mayer, *J. Phys. Chem.*, 1969, **73**, 3941.

[8] W. A. Pryor, 'Free Radicals,' McGraw-Hill, New York, 1966, p. 75.

[9] A. Padwa, *Tetrahedron Letters*, 1964, 3465.

[10] A preliminary report has been published, C. M. Previtali and J. C. Scaiano, *Chem. Comm.*, 1971, 1298.

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

[12] P. J. Wagner and G. S. Hammond, *Adv. Photochem.*, 1968, **5**, 93; S. P. McGlynn, T. Azumi, and M. Kinoshita, 'Molecular Spectroscopy of the Triplet State,' Prentice Hall, New Jersey, 1969, pp. 105—112; H. L. J. Bäckström and K. Sandros, *J. Chem. Phys.*, 1955, **23**, 2197.

double and single C–O bonds and D is the bond dissociation energy. D(OH) Is defined as the energy necessary to

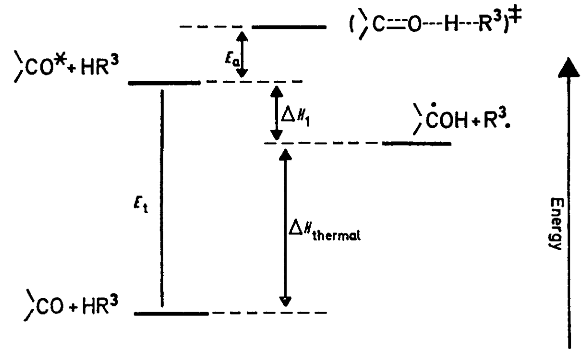
$$\mathrm{RO\cdot} + \mathrm{R^3H} \longrightarrow \mathrm{ROH} + \mathrm{R^3\cdot} \qquad (6)$$

$$\Delta H_1 = E_d - E_t + D(\mathrm{R^3H}) - D(\mathrm{OH}) \qquad (7a)$$

$$\Delta H_6 = D(\mathrm{R^3H}) - D(\mathrm{OH}) \qquad (7b)$$

cleave the O–H bond without forming new bonds or changing the order of already existing ones. This involves considering the double bond contribution to the C=O bond as an independent term. This approach has the advantage of making the O–H bonds in alcohols and ketyl radicals comparable and has been frequently used.[13] ΔH_1 and the enthalpy change for the analogous thermal reaction are related by $\Delta H_{\text{thermal}} - E_t = \Delta H_1$.

The Scheme shows the relationships between the different thermochemical parameters involved. The main differences between the hydrogen abstraction reactions of ketone triplets and those of *true* free radicals (*e.g.* alkoxy radicals) can be summarized as follows: (*a*) the presence of two unpaired electrons instead of one; (*b*) the electronic excitation energy; (*c*) the fact that the C–O bond order in the carbonyl compound is not unity.

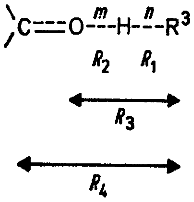


SCHEME

The first point will be taken into account by introduction of the corresponding repulsive term (see below). Points (*b*) and (*c*) can be taken into account simultaneously if one assumes that the essential role of E_t is to decrease the C=O bond order. As pointed out above, this is reasonable from the electronic point of view (the π^* orbital being half filled). In addition, the values of E_t and E_d are frequently very similar (*e.g.* they differ by *ca.* 1 kcal mol^{-1} for acetophenone). However E_t and E_d are not 'identical'. This is reflected in the enthalpy change by the presence of the term $E_d - E_t$. One can expect a similar effect along the reaction coordinate. Therefore, we include in the potential energy function the term $(E_t - E_d)m$. This term is usually small and fulfills the requirement of equation (7a) that $V = 0$ for $n = 1$ and $V = \Delta H_1$ for $m = 1$ and can be taken to mean that the energy difference $(E_t - E_d)$ is either provided or evolved *during* the course of the reaction (depending on whether $E_d \gtrless E_t$).†

Of the two unpaired electrons in the carbonyl triplet, one is located on the oxygen atom and will contribute with a Sato's type repulsion term.[14] The other unpaired electron is rather far removed from the reaction centre, and although it can be expected to contribute with a similar term,[3] the actual energy contribution will be small due to the large value of r_4 (see later).

In accordance with these assumptions, expression (8) gives the potential energy along the reaction co-ordinate,



where $V_{\text{rep}'}$ is the repulsion term [obtained from equations (9) and (10)] due to the electron located near the carbon atom, where δ is the distance from the oxygen atom to the centre of the distribution for the second unpaired electron. The role of this parameter is discussed in detail below.

$$V = E_1 - E_1 n^p - E_2 m^q - (E_t - E_d)m + V_{\text{rep}} + V_{\text{rep}'} \qquad (8)$$

$$V_{\text{rep}'} = \tfrac{1}{2}E_4 \exp(-\beta r_4)[1 + \tfrac{1}{2}\exp(-\beta r_4)] \qquad (9)$$

$$r_4 = R_1 + R_2 + \delta - R_{4s} \qquad (10)$$

The application of transition-state theory as discussed above implies that the reactant molecules are in thermal equilibrium,‡ and that the process is adiabatic.[15] According to Dougherty's classification,[16] it should be regarded as an N-type process. The two radicals produced are expected to have parallel spins; the evidence so far accumulated suggests that this is true in both inter- and intra-molecular hydrogen abstraction.[17]

Evaluation of Rate Constants.—The potential energy profile evaluated using equation (8) can be combined with a suitable version of transition-state theory in order to evaluate pre-exponential factors. We have used the *local-bond-properties* treatment in order to evaluate the rate constants, a technique frequently employed in connection with the B.E.B.O. method.[11] For a three particle model the rate constant is given by

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† A more general form of this term would be $(E_t - E_d)m^r$, but, for simplicity and due to the lack of information about the possible values of r, it has been assumed to be unity.

‡ This is very important for gas-phase reactions at low pressures, since vibrationally 'hot' triplets can be produced in the crossover from the singlet state.

[13] *E.g.*, R. Walsh and S. W. Benson, *J. Amer. Chem. Soc.*, 1966, **88**, 3480.

[14] S. Sato, *J. Chem. Phys.*, 1955, **23**, 592, 2465.

[15] K. J. Laidler, 'The Chemical Kinetics of Excited States,' Oxford University Press, London, 1955, pp. 28 and 88; K. J. Laidler, 'Theories of Chemical Reaction Rates,' McGraw-Hill, New York, 1969, p. 13.

[16] R. C. Dougherty, *J. Amer. Chem. Soc.*, 1971, **93**, 7187.

[17] M. B. Rubin, *Tetrahedron Letters*, 1969, 3361; L. M. Stephenson, P. R. Cavigli, and J. L. Partlett, *J. Amer. Chem. Soc.*, 1971, **93**, 1984; L. M. Stephenson and J. I. Braumann, *ibid.*, p. 1988, and references therein.

equation (11) where the rate constant k is obtained in

$$k = B_e B_\sigma B_\Gamma \left[\left(\frac{R^\ddagger}{R}\right)_l^2 \cdot \left(\frac{F}{F^\ddagger}\right)_l^2 \right] \frac{\omega^*}{1000\,\omega} (R_2{}^2 l_2)_\ddagger l_\phi{}^2 \,. \exp(-V^*/RT) \,. 1{\cdot}81 \times 10^{10} \quad (11)$$

l mol^{-1} s^{-1}. V^* Is the potential energy in the transition state, l_2 and l_ϕ are classical vibrational amplitudes $l_i = (2\pi \boldsymbol{k}T/F_i)^{\frac{1}{2}}$ in units of cm for stretching amplitudes and in radians for bendings; ω^* is the imaginary frequency (cm^{-1}) associated with the reaction co-ordinate; ω is the diagonalization function of the F matrix for a three-particle activated complex (see ref. 11, pp. 71 and 133); B_e represents the ratio of the electronic partition functions of the transition state to those of the reactants, and is unity for an adiabatic process of the type considered here; B_σ is defined as the number of identical reaction paths, and was taken as the number of equivalent reactive hydrogen atoms in the substrate;§ B_Γ is a unitless ratio of quantum corrections of the vibrational degrees of freedom, including the tunnelling correction for the reaction co-ordinate, and is given by equation (12)

$$B_\Gamma = [(\prod_i \Gamma_i^\ddagger)\Gamma^*]/\prod_i \Gamma_i \qquad (12)$$

$$\Gamma_i = (\tfrac{1}{2}u_i)/\sinh(u_i/2); \quad u_i = h\nu_i/\boldsymbol{k}F \qquad (13)$$

where Γ_i is the quantum correction for the ith degree of freedom, and Γ^* is the tunnelling correction, which was calculated as $\Gamma^* = (1 - u^{*2}/24)$ where $|u^*| = h|\omega^*|/\boldsymbol{k}T$ (ref. 18). This is only a first approximation to the quantum correction and its validity has been previously discussed.[19] We feel that the simplicity of this kinetic model does not justify the use of more sophisticated methods. Other symbols have their conventional meaning.[11]

Equation (11) gives the rate constants for a three-particle model; these were corrected to account for a four-particle model, which has been discussed before[6] and can be expected to lead to reasonable estimates; the correction factor is $l_c{}^2/4\pi$ where l_c is the classical vibrational amplitude (in radians) between the C–O bond and the O–H bond in the transition state,[6] taking $F^0(\mathrm{C \cdots O \cdots H}) = 0{\cdot}33 \times 10^{-11}$ erg rad^{-2}.

The Role of δ.—The parameter δ will determine the *weight* of $V_{\mathrm{rep'}}$ to the potential energy profile; therefore, its value should be carefully assigned. In principle, the position of the centre of electron density for the second unpaired electron will change along the reaction co-ordinate.

In the product (ketyl radical) the unpaired electron distribution can be estimated from the e.s.r. parameters by application of equation (14),[20,21] where $Q_{\mathrm{H}}{}^{\mathrm{Me}}$ is a

$$\rho_\alpha = a_{(\beta\text{-Me})}/Q_{\mathrm{H}}{}^{\mathrm{Me}} \qquad (14)$$

constant of value 2·93 mT, $a_{(\beta\text{-Me})}$ is the coupling constant for a radical of the type $\mathrm{Me\dot{C}X^1X^2}$ and ρ_α is the spin density at the carbon atom. For example, for the ketyl radical from acetone $a_{(\beta\text{-Me})} = 1{\cdot}92$ mT (ref. 22) and ρ_α can be estimated as 0·66; if the other 34% of the electron density was fully located on the oxygen atom, then δ_{ketyl} *ca.* 1·0 Å, while the upper limit would be the bond distance, *i.e.* $\delta_{\mathrm{ketyl}} = 1{\cdot}43$ Å. In addition, it has been recently determined that the absorption spectra of ketone triplets (n–π^*) and ketyl radicals are frequently very similar,[23,24] suggesting that the distribution of one electron is not largely affected by the presence of the other one (at the same time this observation supports the biradical model for the carbonyl triplet).

The most realistic approach would probably be to let δ change along the reaction co-ordinate, from its value in the triplet to its final value in the ketyl radical. We have found that this is complicated and cannot be expected to have a very large effect on the kinetic parameters. We have preferred to use a fixed value of δ. The value chosen was the one which seemed most reasonable in the ketyl radical, *i.e.* 1·2 Å (which is about the arithmetic mean between the two extreme cases presented above). This value is likely to be an overestimate of δ in the early stages of the reaction (*i.e.* near the triplet configuration). Therefore the larger error in $\delta^\ddagger$ will be introduced for small values of $m^\ddagger$ (very exothermic reactions). Fortunately, under these conditions the contribution of $V_{\mathrm{rep'}}$ to V^* is small, the latter being rather insensitive to small variations in δ. This is due to the fact that the repulsive terms (V_{rep} and $V_{\mathrm{rep'}}$) reach a maximum for $m = \frac{1}{2}$, but their contribution at the saddle point is far smaller when the transition state resembles either the reagents or the products.†

We have therefore used $\delta = 1{\cdot}2$ Å in all our calculations; however, a series of potential energy profiles were evaluated for other reasonable values of δ, allowing also for displacements perpendicular to the $\mathrm{O \cdots H \cdots C}$ axis. The results of these calculations for benzophenone triplets reacting with a typical C–H bond ($D = 91$ kcal mol^{-1}) are shown in Table 1, from which it is clear that although the model can be further refined by allowing δ to change along the reaction co-ordinate this cannot be

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§ In some examples, such as cyclohexane, the question may arise on whether the 12 hydrogens are equally reactive or whether axial and equatorial atoms have different reactivity. In this particular example, B_σ was taken as 12, due to lack of information, but this should not be taken to mean that axial and equatorial positions have identical reactivity.

† We are grateful to a referee for calling our attention to the importance of a realistic choice of δ. Our previous calculations[10] were based on a larger value of δ and therefore some small differences can be expected with those reported here.

[18] Ref. 11, pp. 83 and 134.

[19] S. G. Christov and Z. L. Georgiev, *J. Phys. Chem.*, 1971, **75**, 1748.

[20] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

[21] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc.* (*A*), 1971, 124, and references therein.

[22] J. Q. Adams, *J. Amer. Chem. Soc.*, 1968, **90**, 5363; J. Q. Adams and R. Ingersoll, *Abs. Amer. Chem. Soc. Meetings*, 1969, **157**, PETR-002.

[23] H. Lutz, personal communication; H. Lutz and L. Lindqvist, *Chem. Comm.*, 1971, 493.

[24] R. Bensassob and E. J. Land, *Trans. Faraday Soc.*, 1971, **67**, 1904, and references therein.

expected to lead to significant changes in the Arrhenius parameters.

TABLE 1

Effect of variations in the position of the unpaired electron located near the carbon atom upon the activation energy

δ [a]	y [a,b]	V^* [c]
0·90	0	6·59
1·00	0	6·42
1·10	0	6·30
1·20	0	6·20
1·30	0	6·12
1·50	0	5·99
1·90	0	5·85
1·20	0·30	6·19
1·20	0·70	6·14
1·20	1·00	6·09
1·50	0·30	5·98
1·50	1·00	5·93

[a] In Å. [b] Displacement perpendicular to the O · · · H · · · C axis; when $y \neq 0$, r_4 was evaluated from the vector sum: $\bar{r}_4 = \bar{R}_1 + \bar{R}_2 + \bar{\delta} + \bar{y} - \bar{R}_{4s}$. [c] In kcal mol⁻¹, calculated excluding ZPE correction, using $E_t = 68{\cdot}7$ and D(CH) = 91 kcal mol⁻¹.

In general the contribution of $V_{rep'}$ is around 9% of the contribution of V_{rep}.

Potential Energy Profiles.—The similarities in the behaviour of ketone triplets and alkoxyl radicals have been pointed out in a variety of reactions,[25] and in some cases these similarities have been extended to hydroxyl radicals.[26] Therefore it seems interesting to compare the potential energy profiles for the reaction of alkoxyl radicals, hydroxyl radicals, and ketone triplets with the same substrate. This comparison is shown in Figure 1, where the triplet energies have been chosen to correspond to acetone, acetophenone, and benzophenone.† The similarities between alkoxyl radicals and ketone triplets are due to similarities in the *shape* of the reaction path in addition to the size of the potential energy barrier. In the case of acetone it seems reasonable to expect an intermediate reactivity between those of alkoxyl and hydroxyl radicals. If this can be taken to mean that the whole potential energy surfaces are similar, then the deuterium isotope effects can also be expected to be of the same order of magnitude.

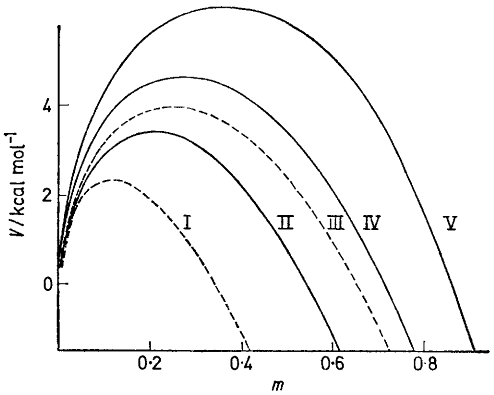

FIGURE 1 Potential energy profiles for the abstraction of a hydrogen atom bonded to carbon (D = 91 kcal mol⁻¹) by I, OH radicals; II, acetone triplets; III, alkoxyl radicals; IV, acetophenone triplets; V, benzophenone triplets

Figure 2 shows the role of the different parameters in equation (8) in determining the shape and height of the potential energy profile.

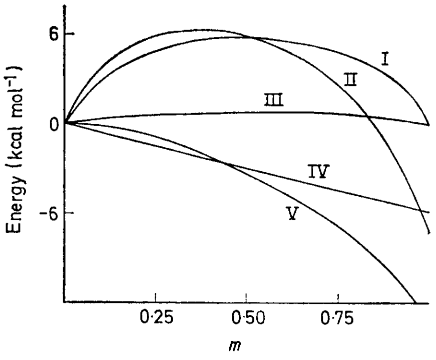

FIGURE 2 Role of the different factors in equation (8), I, V_{rep}; II, V; III, $V_{rep'}$; IV, $+(E_t - E_d)m$; V, $(E_1 - E_1n^p - E_2m^q)$, using the same parameters as in Figure 1, curve V

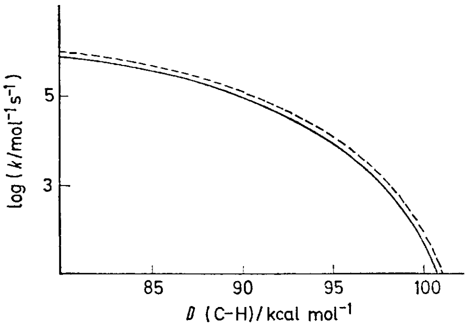

FIGURE 3 Calculated rate constants for the abstraction of a hydrogen atom by benzophenone triplets from a substrate having only one reactive hydrogen atom. The dotted line excludes ZPE correction, whilst the full line includes it

Zero-point Energy Corrections.—The values of E_1 and E_2 to be used in equation (8) should be bond dissociation energies corrected to 0 K and by zero point-energies (ZPE). The latter was evaluated as $\frac{1}{2}h\nu$ where ν is the vibrational frequency of the bond being dissociated. This is not strictly equivalent to ZPE, but in the absence of better data we think that this is a reasonable estimation of it. We have calculated the rate constants for the abstraction by benzophenone from a hypothetical substrate (molecular weight = 120) having only one reactive hydrogen atom. The results, including and excluding ZPE correction are shown in Figure 3, from which it may be seen that although ZPE values are

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† Other molecular parameters employed are: $\beta_3 = 2{\cdot}05$ Å⁻¹; $E_3 = 85{\cdot}4$ kcal mol⁻¹; $R_3 = 1{\cdot}43$ Å; D(OH) = 104 kcal mol⁻¹; R(OH) = 0·97 Å; D(CH) = 91·0 kcal mol⁻¹; R(CH) = 1·09 Å; $E_d = 74{\cdot}6$ kcal mol⁻¹; $\delta = 1{\cdot}20$ Å.

[25] C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, 1965, **87**, 3361; P. J. Wagner, *Accounts Chem. Res.*, 1971, **4**, 168; A. G. Davies, D. Griller, B. P. Roberts, and J. C. Scaiano, *Chem. Comm.*, 1971, 196; A. G. Davies, B. P. Roberts, and J. C. Scaiano, *J. Chem. Soc.* (*B*), 1971, 2171; D. R. Arnold, R. I. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1964, 1425.

[26] M. Nakashima and E. Hayon, *J. Phys. Chem.*, 1971, **75**, 1910.

certainly important in the calculation of isotope effects, the exclusion of this correction will not introduce large differences for most organic reactions. Hereafter, wherever the symbol D replaces E, the ZPE correction is excluded.

Regarding deuterium isotope effect, the only measurement of which we know is of the reaction of benzophenone triplets with diphenylmethanol and [$^2H_1$]-diphenylmethanol for which $k_H/k_D = 2{\cdot}7$ (ref. 27) in benzene. The estimated value is 2·1 which includes a tunnelling correction and corresponds to the gas phase.

The Acetone–Hydrogen Bromide System.—O'Neal and Larson [28a] have measured the kinetic parameters for reaction (15) in the gas phase, and obtained $k_{15}/\text{l mol}^{-1}\text{ s}^{-1} = 10^{9{\cdot}25 \pm 0{\cdot}65} \exp(-0{\cdot}35 \pm 1{\cdot}1/RT)$ with R in kcal

$$\text{Me}_2\text{CO}^* + \text{HBr} \longrightarrow \text{Me}_2\dot{\text{C}}\text{OH} + \text{Br}\cdot \qquad (15)$$

mol^{-1} K^{-1}. In the same publication they suggest $k_{15}/\text{l mol}^{-1}\text{ s}^{-1} = 10^{9{\cdot}6}\,.\exp(-1{\cdot}1/RT)$.

We have performed a series of calculations for this system using the B.E.B.O. method and obtained $k_{15}/\text{l mol}^{-1}\text{ s}^{-1} = 10^{9{\cdot}49}\,.\exp(-0{\cdot}37/RT)$, a value which is in remarkably good agreement with experiment. Although this agreement should not be overemphasized because it may be partly accidental, the result is certainly encouraging. Some parameters of the activated complex (*e.g.* $F_{\text{bend}} = 0{\cdot}778 \times 10^{-13}$ erg rad^{-2}) raise doubts regarding the application of separability of internal degrees of freedom implicit in this formulation of transition-state theory. Structural parameters of the reactants and the transition state can be seen in Table 2.†

TABLE 2

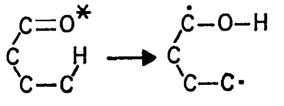
Structural parameters for reaction (15)

Property [a]	Units	Reactants	Products	Activated complex
$m^{\ddagger}$		0·0	1·0	0·017
V^*	kcal mol^{-1}			0·37
R_1	Å	1·42		1·425
R_2	Å		0·97	1·987
F_{11}	dyn cm^{-1}	$3{\cdot}90 \times 10^5$		$2{\cdot}84 \times 10^5$
F_{22}	dyn cm^{-1}		$7{\cdot}5 \times 10^5$	$-0{\cdot}214 \times 10^5$
F_{bend}	erg rad^{-2}			$0{\cdot}77 \times 10^{-13}$
ω^*	cm^{-1}			34·8 i
ω_{str}	cm^{-1}	(2587)	(3000)	2650
ω_{bend}	cm^{-1}			139
B(T) [b]	l mol^{-1} s^{-1}			$10^{9{\cdot}49}$
D	kcal mol^{-1}	86·7	104·0	
ZPE	kcal mol^{-1}	3·8	4·0	
Γ_{str}		0·024		0·028
Γ_{bend}				0·981
Γ^*				1·10

[a] Other parameters: $E_3 = 56{\cdot}5$ kcal mol^{-1}; $R_{3s} = 1{\cdot}77$ Å; $\beta_3 = 2{\cdot}25$ Å^{-1}. [b] Four-particle model.

Comparison with an Alternative Model.—Before comparing alternative models we will outline the main characteristics of the present one. (*a*) The shape of the potential energy surface, and the height of the barriers are mainly determined by energy factors [see equation (8)]. (*b*) All arguments used herein are only valid for n–π^* states, *i.e.* $E_{(^3\pi-\pi^*)} - E_{(^3n-\pi^*)} \gg kT$. (*c*) The main role of the triplet state energy is to provide the energy difference between double and single C–O bonds. (*d*) The formation of the O–H bond is simultaneous with the cleavage of the R^3–H bond. (*e*) The reaction is adiabatic and proceeds with spin conservation. (*f*) The unpaired electron on the oxygen atom can be considered as the active electron, while the other one makes a small energy contribution. In fact, if the electronic distribution in the singlet and triplet states are similar, one can expect a similar model (excluding $V_{\text{rep}'}$) to hold for singlet-state hydrogen abstraction. In general one would predict singlet-state reactions to be faster than triplet-state ones due to the decrease in repulsion and the increase in electronic energy. (*g*) In principle the method is only applicable to gas-phase reactions; however, some approximations can be carried out which allow its use for reactions in solution; these are discussed in the following paper.[29]

Hammond [30] has pointed out that chemical reactions involving excited species are special forms of radiationless transitions. Heller [31] has also used this concept for several types of hydrogen-transfer reactions, including intermolecular abstraction [reaction (1)] and 1,4-biradical formation, reaction (16).



(I) (16)

Heller has suggested that an electronic-to-vibrational energy transfer takes place as a discrete step, this vibrational energy being selectively localized in R^3–H stretching modes prior to the production of radicals and the formation of the O–H bond. This electronic relaxation must leave the carbonyl compound its lowest singlet state; therefore, the products in reaction (1) and the 1- and 4-positions in (I) should have antiparallel spins, independent of the electronic state from which they were formed. This prediction is different from the one from the biradical model [see (*e*) above]. The evidence so far accumulated suggests that the reaction proceeds with spin conservation,[17] and differences in the properties of 1,4-biradicals, depending on their origin are common.[17,32]

Tin–hydrogen bonds are known to be far more reactive than carbon–hydrogen bonds,[33] and this behaviour

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† More recently, the same laboratory has reported kinetic data for the reaction of acetone triplets with silane. They estimated an activation energy of 3·4 kcal mol^{-1}.[28b] Our estimated value for this system is *ca.* 2·4 kcal mol^{-1}.

[27] W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, 1961, **83**, 2789.

[28] (*a*) C. W. Larson and H. E. O'Neal, *J. Phys. Chem.*, 1966, 2475; (*b*) E. H. O'Neal, S. Pavlou, T. Lubin, M. A. Ring, and L. Batt, *J. Phys. Chem.*, 1971, **75**, 3945.

[29] C. M. Previtali and J. C. Scaiano, *J.C.S. Perkin II*, following paper.

[30] G. S. Hammond, *Adv. Photochem.*, 1969, **7**, 373.

[31] A. Heller, *Mol. Photochem.*, 1969, **1**, 257.

[32] I. Fleming, A. V. Kemp-Jones, and E. J. Thomas, *Chem. Comm.*, 1971, 1158.

[33] D. R. G. Brimage, R. S. Davidson, and P. F. Lambeth, *J. Chem. Soc.* (*C*), 1971, 1241.

was associated to the weakness of the tin–hydrogen bond, in full agreement with the predictions using the modified B.E.B.O. method.[29] However, in Heller's model the prediction would be that 'the most reactive bonds are those that have high vibrational frequencies'. Even allowing for changes in anharmonicity it seems unlikely to be able to justify the much larger reactivity of Sn–H bonds having vibrational frequencies in the range of 1850 cm^{-1} (ref. 34), compared with *ca.* 3000 cm^{-1} for C–H bonds.[35] A similar argument holds in discussing the high reactivity of boron-carbon bonds.[25c,d,36]

If the rate-determining step for reactions (1) and (16) can be regarded as an electronic-to-vibrational energy transfer, then, we find it difficult to correlate the low reactivity of $^3\pi$–π^* states with the enhancement of radiationless transitions which accompanies the vibrational coupling between n–π^* and π–π^* states observed in aromatic carbonyl compounds.[37]

Dougherty[15] has recently reported a perturbation molecular orbital treatment for several types of photochemical reactions. Our model is consistent with his treatment; in fact it could be considered that the application of the B.E.B.O. method involves the assumption of a particular barrier shape for the group of N-type reactions considered here.

Conclusion.—From the above discussion and the agreement between experimental and calculated kinetic parameters observed in both the gas phase and in solution,† we conclude that the best available interpretation of reaction (1) is that of considering the ^3n–π^* state of carbonyl compounds as a biradical, where the oxygen atom behaves as a true free radical centre.

The extended version of the B.E.B.O. method discussed above provides a way of predicting the kinetics of these reactions, while mantaining the main characteristics of Johnston and Parr's original method,[2] *i.e.* no setting of parameters is necessary and all the empiricism is completely outside the field of chemical kinetics. Moreover, the practical application of the method involves little, if any 'extra' difficulty compared with the application of the B.E.B.O. method to reaction (2).

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† For a comparison with results in solution and a discussion of the organic aspects of the reaction see Part II.[29]

[34] E. J. Kupchik in 'Organotin Compounds,' vol. 1, ed. A. K. Sawyer, Marcel Dekker, New York, 1971, p. 17.

[35] *E.g.*, T. Schimanouchii, 'Tables of Molecular Vibrational Frequencies,' Part I, National Bureau of Standards, NSRDS-NBS 6, Washington, 1967.

[36] M. V. Encina and E. A. Lissi, *J. Organometallic Chem.*, 1971, **29**, 21.

[37] E. C. Lim and Y. H. Li, *Chem. Phys. Letters*, 1969, **4**, 25; E. C. Lim, Y. H. Li, and R. Li, *J. Chem. Phys.*, 1970, **53**, 2443.