The Kinetics of Photochemical Reactions. Part II.[1] Calculation of Kinetic Parameters for the Intermolecular Hydrogen Abstraction Reactions of the Triplet State of Carbonyl Compounds

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By application of a novel method based on the Bond-Energy–Bond-Order method, a series of kinetic parameters for reactions involving hydrogen abstraction by carbonyl triplets have been calculated. In principle the method is only applicable in the gas-phase; however, a good agreement with experiment is generally observed in reactions involving $n-\pi$* triplets in non-polar solvents. The possibility of using the method for carbonyl compounds having low lying $\pi-\pi$* triplets is discussed. A series of pre-calculated kinetic parameters are reported in order to allow the fast estimation of rate constants avoiding detailed calculations.

THE Bond-Energy–Bond-Order (B.E.B.O.) method allows the calculation of kinetic parameters for many processes involving hydrogen abstraction;[2] in previous papers [1,3] we have reported a method based on it which allows the calculation of kinetic parameters for the hydrogen abstraction reactions of the triplet state of carbonyl compounds [reaction (1)].

$$R^1R^2CO^* + R^3H \longrightarrow R^1R^2COH + R^3\cdot \qquad (1)$$

In principle, the applicability of this method is restricted to gas-phase reactions. We feel that the method would be of little practical value if it were not applicable in solution and if it were not readily accessible to the organic photochemist. We aim in this paper to (a) discuss the conditions under which the method might

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[1] Part I, C. M. Previtali and J. C. Scaiano, preceding paper.

[2] *E.g.*, H. S. Johnston and C. Parr, *J. Amer. Chem. Soc.*, 1963, **85**, 2544; S. W. Mayer and L. Schieler, *J. Phys. Chem.*, 1968, **72**, 236; E. Lissi, M. Passeggi, and C. Previtali, *Anales Asoc. quim. Argentina*, 1970, **58**, 167.

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

be applied to reactions in solution; (b) provide a series of precalculated kinetic parameters in order to allow the fast estimation of a rate constant without going into detailed calculations; (c) point out the limitations of this model and how some of these, such as the applicability to ketones having low lying $\pi-\pi^*$ triplets, can be sorted out; and (d) show a comparison between calculated and experimental rate constants for reactions in solution.

In order to avoid unnecessary repetition some of the physico-chemical aspects (already discussed in Part I [1]) are excluded from this paper and only the rather more organic aspects are considered.

then the ratio of rate constants for the substrates (1) and (2) can be evaluated using equation (2).

$$\frac{k_1}{k_2} = \frac{\exp{(-E_{a1}/RT)}}{\exp{(-E_{a2}/RT)}} \cdot \frac{(\text{no . H})_1}{(\text{no . H})_2} \qquad (2)$$

A comparison of calculated and experimental rate constants using equation (2) has already been published.[3] The method can be improved by also evaluating the ratio of pre-exponential factors.

The calculated absolute rate constants can generally be expected to be mainly independent of the phase,† since they correspond to reactions between neutral

TABLE 1

Comparison between experimental and calculated rate constants at ca. 25°

No.	Ketone	Substrate [a]	$D(R^3-H)$ [b]	Solv.[c]	E_a [b,d]	log k_{exp} [e]	log k_{calc}.
(1)	Acetophenone [g]	Isopropanol (1)	88	B	3·70	6·26 [h]	5·73
(2)	Benzophenone [g]	Isopropanol (1)	88	B	5·01	6·04 [h]	5·42
(3)	Benzophenone [i]	Isopropanol (1)	88	N	5·01	6·11	5·42
(4)	Benzophenone [j,k]	Cyclohexane (12)	94	N,C	7·60	5·56	5·33
(5)	Benzophenone [j,k]	Ethanol (2)	91	N	6·19	5·75	5·27
(6)	Benzophenone [l,m]	2,3-Dimethylbutane (2)	91	B	6·19	5·51 [m]	5·27
(7)	Benzophenone [l]	Octan-2-ol (1)	88	B	5·01	6·20 [m]	5·42
(8)	Benzophenone [n]	t-Butylbenzene (9)	97	(B?)	9·22	5·01 [o]	4·45
(9)	Benzophenone [j,k]	Dioxan (8)	91	N	5·19	5·63	4·97
(10)	Acetophenone [p,k]	Cyclohexane (12)	94	N,C	5·66	5·68	6·21
(11)	Acetophenone [n]	t-Butylbenzene (9)	97	(B?)	7·14	4·85 [q]	5·45
(12)	Benzophenone [r]	Bu$_4^n$Sn (8)	94	B	7·60	5·85	5·16 [s]
(13)	Benzophenone [r,t]	Bu$_3^n$SnH (1)	70	B	2·07	7·68	6·90 (7·52)
(14)	Acetone [t,u]	Bu$_3^n$SnH (1)	70	H	1·68	8·30 [v]	7·51 (7·92)
(15)	Pyruvic acid [w,x]	Methanol (3)	94	B	7·50	5·70	4·86
(16)	Pyruvic acid [w,x]	2-Methylpropanol (2)	90	B	5·94	6·25	5·31
(17)	Benzophenone [l]	Toluene (3)	85	B	4·16	5·22 [m]	6·07
(18)	Benzophenone [l]	Isopropylbenzene (1)	79	B	2·70	5·60 [m]	6·17
(19)	Benzophenone [n]	Ethylbenzene (2)	82	(B?)	3·30	5·63 [v]	6·24
(20)	Acetophenone [p,k]	Toluene (3)	85	N	3·09	5·37	6·49

[a] The number of reactive hydrogen atoms is given in parentheses. [b] kcal mol^{-1}. [c] Key: B = benzene, C = cyclohexane, N = neat substrate, H = hexane. [d] Unless otherwise indicated calculated using $D(O-H) = 104$ kcal mol^{-1}, $E_d = 74·6$ kcal mol^{-1}, $\beta_3 = 2·05$ Å^{-1}, $E_3 = 85·4$ kcal mol^{-1}, $R_{1s} = 0·97$ Å, $R_{2s} = 1·09$ Å, $R_{3s} = 1·43$ Å. [e] 1 mol^{-1} s^{-1}. [f] In the gas phase, four-particle model, in 1 mol^{-1} s^{-1}. [g] H. Lutz, M. C. Duval, E. Breheret, and L. Lindqvist, J. Phys. Chem., 1972, 76, 821. [h] Value extrapolated to zero substrate concentration. [i] A. Beckett and G. Porter, Trans. Faraday Soc., 1963, 59, 2038. [j] G. Porter and M. R. Topp, Proc. Roy. Soc. A, 1970, 315, 163. [k] The original paper gives the unimolecular rate constant in neat substrate. [l] C. Walling and M. C. Gibian, J. Amer. Chem. Soc., 1965, 87, 3361. [m] Using competitive data from the reference given and comparing with the data in line 4. [n] A. Padwa, Tetrahedron Letters, 1964, 3465. [o] Absolute rate constant estimated by comparison of the competitive data with the value in line 6. [p] Ref. 7. [q] The relative rate constant given in the original publication was compared with the one in line 20. [r] D. R. G. Brimage, R. S. Davidson, and P. F. Lambeth, J. Chem. Soc. (C), 1971, 1241, the authors assume $k_d = 3 \times 10^5$ s^{-1}. [s] If the number of reactive hydrogen atoms is taken as 24, log k (calc) = 5·64. [t] The parameters used for Sn−H bonds are $\beta_3 = 1·74$ Å^{-1}; $E_3 = 71$ kcal mol^{-1}, $R_3 = 2·16$ Å. The actual value of β_3 is uncertain. The values of log k given in parentheses are approximate values using $\beta_3 = 2·04$ Å^{-1}. [u] P. J. Wagner, J. Amer. Chem. Soc., 1967, 89, 2503. [v] The reported value was 8×10^8 1 mol^{-1} s^{-1} based on k_q (diff. quench.) = 10^{10} 1 mol^{-1} s^{-1}. The value in the Table was recalculated using $k_q = 2·4 \times 10^9$ 1 mol^{-1} s^{-1}, ref. 7. [w] P. B. Ayscough and R. C. Sealy, personal communication. Determined by e.s.r. spectroscopy. [x] $(E_t - E_d)$ Assumed as $-6·5$ kcal mol^{-1} (see text). [y] The original competitive data were compared with the rate constant in line 18.

Application of the Model to Reactions in Solution.— Most of the photochemical reactions involving hydrogen transfer have been studied in solution; therefore this is the field where any kinetic model would be most useful. We have already suggested a very simple version allowing the comparison of rate parameters in solution.[3] If one assumes that a ratio of rate constants for two similar reactions will be independent of the phase * and that the pre-exponential factors will be proportional to the number of reactive hydrogen atoms present in the substrate and independent of any other parameters,

* The constancy of disproportionation–combination ratios provides an excellent example.[4]
† Provided that the solvent does not affect the relative positions of the $^3n-\pi^*$ and $^3\pi-\pi^*$ levels.[5]

species.[6] Table 1 shows a comparison between gas-phase calculated rate constants and experimental values in solution for a series of hydrogen abstractions, most of them in non-polar solvents.

Quite often the values reported by different laboratories involve different assumptions, techniques, and

[4] P. S. Dixon, A. P. Stephani, and M. Szwarc, J. Amer. Chem., 1963, 85, 2551; C. M. Blackman, S. Claesson, and M. Szwarc, Trans. Faraday Soc., 1970, 66, 3061.
[5] H. Lutz, M. C. Duval, E. Breheret, and L. Linqvist, VI International Conference on Photochemistry, Bordeaux, 1971, abstract no. 19; R. Rusakowicz, G. W. Byers, and P. A. Leermakers, J. Amer. Chem. Soc., 1971, 93, 3263.
[6] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' Wiley, New York, 1963, 2nd edn., p. 128; S. W. Benson, ' The Foundations of Chemical Kinetics,' McGraw-Hill, New York, 1960, p. 507.

solvents. This frequently makes it difficult to compare calculated and experimental rate parameters. In those cases where only competitive data were available, or when rather unusual assumptions were involved, we have estimated the absolute rate constants by comparing the competitive data with rate parameters determined by a laser technique or by quenching by dienes, for which the rate of quenching is well known.[7]

The agreement of the rate constants is generally very good. For the reaction of acetophenone triplets with isopropanol the experimental activation energy is $2 \cdot 92$ kcal mol^{-1}, determined in the 20—80° range by the nanosecond laser technique,[8] which is also in reasonably good agreement with our calculated value. The last four lines in Table 1 show the results for reactions where R$^{3 \cdot}$ is centred on a carbon atom vicinal to an aromatic ring. Here, the calculated values are consistently high. This is not surprising, since, for instance reaction (4) is five times faster than reaction (5)[9] at 60°, although the

$$\text{Me}^{\cdot} + \text{Me}_2\text{CHCHMe}_2 \longrightarrow \text{CH}_4 + \text{Me}_2\text{CH}\dot{\text{C}}\text{Me}_2 \qquad (4)$$

$$\text{Me}^{\cdot} + \text{PhMe} \longrightarrow \text{CH}_4 + \text{PhCH}_2^{\cdot} \qquad (5)$$
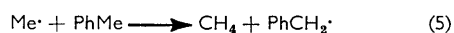
C–H bond in toluene is ca. 6 kcal mol^{-1} weaker than in 2,3-dimethylbutane. This type of 'anomalous' behaviour is probably due to the fact that for very exothermic reactions the transition state structure is rather close to that of the reagents, so that, although the products are highly stabilized by resonance, this effect is negligible in the transition state.[10,11] We feel that for this type of reaction use of equation (2), or the full evaluation of the ratio of rate constants is better than the evaluation of absolute rate constants. It should be noticed that the ratios of rate constants are in reasonable agreement with the experimental data. Application of equation (2) for benzophenone triplets predicts a reactivity ratio of $1 : 2 \cdot 1 : 3 \cdot 3$ for toluene : ethylbenzene : isopropylbenzene.

Pyruvic acid has a reactivity similar or slightly higher than that of benzophenone[12] although its triplet energy is probably 3 or 4 kcal mol^{-1} lower.[13] If one estimates its value of E_d using group additivity rules[14] one finds that this figure is also some 3 kcal mol^{-1} lower than the analogous figure for benzophenone; therefore, the values of $(E_t - E_d)$ are similar for both carbonyl compounds. This clearly exemplifies the idea that the reactivity of the triplet n–π^* state of carbonyl compounds is determined by $(E_t - E_d)$ rather than by E_t. The former can be considered to be its reactivity parameter. The slightly higher reactivity of pyruvic acid can probably be attributed to a larger energy gap between ^3n–π^* and $^3\pi$–π^* states.

Calculated 'Standard' Kinetic Parameters.—Many potentially useful semi-empirical techniques involve

tedious calculations which, in practice lead to their limited use. In this section we intend to give the results of a series of 'standard' calculations in order to allow the estimation of kinetic parameters without detailed calculations. By standard calculations we mean kinetic data evaluated using parameters which are commonplace in this type of reaction. For example, in principle any value is possible for the triplet-state energy but in practice the usual values are reduced to those corresponding to a rather small group of ketones. Of course data obtained in this way cannot replace the amount of information that a detailed calculation can provide (see, e.g. Table 2 in Part I).[1]

The values of log k calculated using the information provided in this section will usually be within $\pm 0 \cdot 2$ of the value obtainable by carrying out the full calculation.

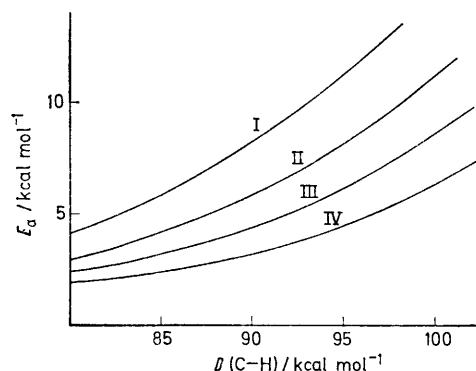(a) *Activation energies.* Figure 1 shows a series of

FIGURE 1 Calculated activation energies for several values of $(E_t - E_d)$, I, $-12 \cdot 0$ kcal mol^{-1}; II, $-5 \cdot 9$ kcal mol^{-1} (benzophenone); III, $-1 \cdot 0$ kcal mol^{-1} (acetophenone); IV, $4 \cdot 4$ kcal mol^{-1} (acetone). All for $D(\text{O–H}) = 104$ kcal mol^{-1}

plots of activation energies for the abstraction of hydrogen atoms bonded to carbon, with bond dissociation energies in the range 80—102 kcal mol^{-1} and for several values of $E_t - E_d$. The bond energies do not include ZPE corrections. The activation energies for other values of E_t can be interpolated making a plot of E_a vs. E_t for the desired value of $D(\text{C–H})$. Extrapolations are not encouraged.

(b) *Structural parameters.* Establishing whether a method is good or not for the prediction of kinetic parameters is one thing, but establishing whether the predicted structure of the transition state is correct is another, and certainly far more risky. Some of these parameters, such as the bond orders in the activated complex cannot be tested or checked, and whether they represent actual parameters of the activated complex or not is usually inferred from predictions of pre-exponential factors, isotope effects, and general trends when the different thermodynamic parameters are changed.

[7] H. Lutz and L. Lindqvist, *Chem. Comm.*, 1971, 493.
[8] H. Lutz, personal communication.
[9] A. F. Trotman-Dickenson and G. S. Milne, 'Tables of Bimolecular Gas Reactions,' National Bureau of Standards, NSRDS-NBS 9, Washington, 1967.
[10] M. Szwarc, *Chem. Soc. Special Publ.*, No. 16, 1962, p. 91.

[11] J. Grotewold, E. A. Lissi, and J. C. Scaiano, *J. Chem. Soc.* (*B*), 1971, 1187.
[12] P. B. Ayscough and R. C. Sealy, personal communication.
[13] P. A. Leermakers, P. C. Warren, and C. F. Vesley, *J. Amer. Chem. Soc.*, 1964, **86**, 1768.
[14] S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1968, ch. II.

These concepts should be kept in mind when using or calculating parameters of the transition state.

Figure 2 shows the calculated values of the bond orders in the transition state for the bonds being formed (left
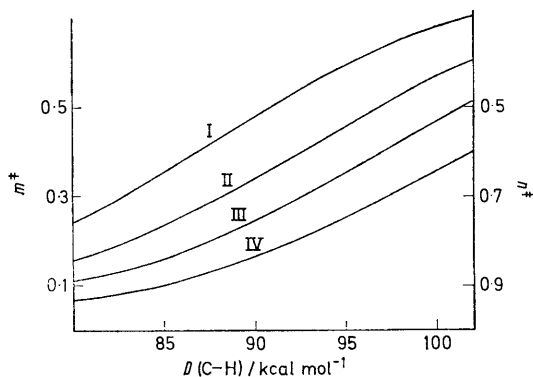

FIGURE 2   Bond orders in the transition state. The curves are labelled as in Figure 1

scale) and broken (right scale). These parameters can be related to bond lengths using equation (6) [12] where R is the bond length, R_s the stable bond length, and n the bond order.

$$R = R_s - 0.6 \log_{10} n \qquad (6)$$

(c) *Pre-exponential factors.* These were evaluated using bond energies which excluded ZPE corrections. The second derivative of V_{rep}' was always neglected; However, a few estimations of its value showed that this does not introduce any important error.*   Figure 3
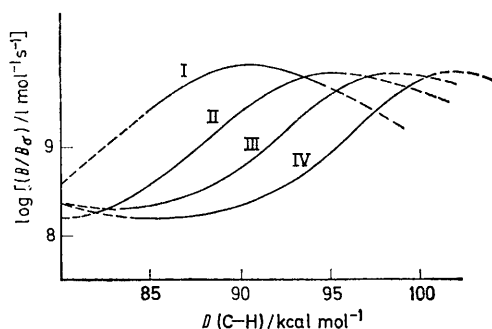

FIGURE 3   Calculated pre-exponential factors. The dashed sections indicate calculations carried out at 3 or 4 kcal mol⁻¹ intervals. The curves are labelled as in Figure 1

shows a series of curves of log (B/B_o) vs. D(C–H) for the same values of $(E_t - E_d)$ as in the previous figures. The pre-exponential factors were calculated using the four-particle model previously discussed,[1,15] and are mainly independent of the molecular weights of the ketone and R³–H provided that both are much greater

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* The meaning of the different symbols is explained in Part I.[1]

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

[16] *E.g.*, J. E. Leffler and E. Grunwald, ' Rates and Equilibria of Organic Reactions,' Wiley, New York, 1963, chs. 6—9.

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than the hydrogen mass.   For the plots of a ' standard substrate ' which was assumed to have only one reactive hydrogen atom and a molecular weight of 120 was used. Table 2 shows an example of the dependance of log B on the molecular weight of the fragments.

TABLE 2

Dependence of pre-exponential factors upon molecular weights [a]

E_t/kcal mol⁻¹	M(ketone)	M(R³–H)	log B/1 mol⁻¹ s⁻¹ [b]
68·7 [d]	182	100	9·483 [c]
68·7	182	150	9·482
68·7	100	100	9·486
73·6 [e]	120	100	8·882
73·6	100	100	8·890

[a] D(C–H) = 91 kcal mol⁻¹. [b] At 298 K, per reactive hydrogen atom. [c] The number of decimal places in this column exceeds the number of significant figures in order to make mass effects more clear. [d] Value corresponding to benzophenone. [e] Value corresponding to acetophenone.

In fact B is the temperature dependent pre-exponential factor. The best way to compare experimental and calculated A factors would be to calculate the rate constants at several temperatures and then to obtain E_a and A from an Arrhenius plot. In general the differences are not large and both procedures are exactly equivalent for rate constant calculations.

Two aspects deserve additional comment. (i) The rate of reactions in solution is limited by the rate of diffusion of the reagents through the solvent. Therefore, the values obtained using Figure 3 can sometimes result in an overestimation of the pre-exponential factor and therefore of the rate constant. In other words, pre-exponential factors in solution can be expected to be less dependent upon D(C–H) than predicted by Figure 3. (ii) Finally, we note that since all the calculations excluded ZPE correction they cannot be used to evaluate kinetic isotope effects.

Some Limitations.—The calculations using the present method are entirely based on thermodynamic and vibrational factors and on the radical-like characteristics of carbonyl triplets. The organic chemist is frequently interested in other factors as well. Quite often a change in these factors does not have the rather drastic effect that changes in thermodynamic parameters have. However, these factors, which include solvent, substituent, and steric effects among others, can throw light on mechanistic details of the reaction. Extensive studies of extra-thermodynamic correlations have been carried out.[16] The method described above cannot be expected to account for any of these effects, unless they can be expressed quantitatively as an effect upon the thermodynamic or vibrational parameters which enter in the calculations.

In the case of reaction (1), two factors deserve special attention. (i) Changes in the oxygen atom charge affect the rate of reaction; this is specially true for heterocyclic ketones.[17]   So far, we do not see any

[17] P. Traynard and J. P. Blanchi, *Compt. rend.*, 1968, **266**, C, 1492, 1511; **267**, C, 1381; P. J. Wagner and G. Capon, *Mol. Photochem.*, 1969, **1**, 173.

explicit way of taking it into account. (ii) The presence of low lying $^3\pi–\pi^*$ states decreases the reactivity of the ketone. This effect has been discussed in detail by Wagner [18] and an inversion of states can be due to solvent [5] or substituent effects.[19] Wagner proposed two alternative models, one based on vibronic mixing of states and the other on equilibration of states. The latter mechanism can be expected to be the most important when the two states are very close together.[18] The simplest correction factor would then be given by application of a Boltzmann distribution [equation (8)]

$$\alpha = \{1 + \exp\left[-(E_t{}^n - E_t{}^\pi)/RT\right]\}^{-1} \quad (8)$$

where $E_t{}^n$ and $E_t{}^\pi$ are the two triplet state energies and α is the factor by which the reactivity of the pure $^3n–\pi^*$ state should be multiplied. For small energy differences α is only slightly temperature dependent; e.g. at 298 K if $(E_t{}^n - E_t{}^\pi) = 2$ kcal mol^{-1}, the change in activation energy would be of only 0·072 kcal mol^{-1} and for most purposes can be neglected. This is in agreement with experiment which has shown that the activation energies for abstraction of the hydrogen from isopropanol by acetophenone and m-methylacetophenone are very similar.[8] Therefore if the energies of both triplet states are known one can still expect to use the B.E.B.O. method, correcting the pre-exponential factor by α. Furthermore, since the effect is only dependent upon the carbonyl compound, equation (2) can be used without any correction. The value of E_t to be used in the calculation of the potential energy profile should always be the one corresponding to the $^3n–\pi^*$ state.

We believe that this method will be useful in organic photochemistry, and hope that more Arrhenius parameters will become available for comparison in the near future.

[18] P. J. Wagner, Accounts Chem. Res., 1971, 4, 168.
[19] N. C. Yang and R. L. Dusenbery, J. Amer. Chem. Soc., 1968, 90, 5899.