A Kinetic Model for the Intermolecular Photoreduction of Carbonyl Compounds; a Novel Application of the Bond-Energy–Bond-Order Method

By C. M. PREVITALI
(*Facultad de Farmacia y Bioquimica, Junin* 956, *Buenos Aires, Argentina*)
J. C. SCAIANO*
(*Christopher Ingold Laboratories, University College London,* 20 *Gordon Street, London* WC1H 0AJ)

Summary The application of the Bond-Energy–Bond-Order method to the reactions of the triplet state of carbonyl compounds provides a way of predicting the selectivities and reactivities of their hydrogen abstraction reactions and supports the radical-like model for them.

THE triplet state of a carbonyl compound is known to exhibit radical-like behaviour, in particular carbonyl triplets and alkoxy radicals show similar reactivities in hydrogen abstraction reactions,[1] Norrish type II photoelimination,[2] substitution at a metal centre,[3] oxetan formation[4] and photoenolization.[5]

The Bond-Energy–Bond-Order (BEBO) method, which is useful in the quantitative description of a large number of hydrogen abstraction reactions,[6] provides a way of testing the free radical model for the intermolecular hydrogen abstraction reactions of carbonyl triplets [reaction (1)].

$$R_2CO^* + AH \longrightarrow R_2\dot{C}OH + A^\cdot \quad (1)$$

The BEBO method has not been applied previously to reactions involving excited species. For a hydrogen atom abstraction process such as (2), where B· has a single unpaired electron, the BEBO method allows the calculation of a potential energy profile using equation (3),

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

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

Here E_1 and E_2 are the bond dissociation energies of the bonds being broken and formed, n and m are the corresponding bond orders ($n + m = 1$), p and q the bond indices, and V_{rep} a Sato's repulsive function.[7,8]

We have assumed that the carbonyl triplet behaves as a biradical (that is two *non*-interacting doublets), and that the triplet state energy (E_t), provides the energy difference between double and single C–O bonds (E_d).† Since E_t and E_d are usually slightly different, a correction term was introduced, assuming that ($E_t - E_d$) is either lost or provided during the course of the reaction. The potential energy can then be calculated using equation (4), where

$$V = E_1 - E_1n^p - E_2m^q - (E_t - E_d)m + V_{rep} + V_{rep}' \quad (4)$$

V_{rep}' is the repulsive term corresponding to the interaction between the second unpaired electron in the carbonyl triplet and the unpaired electron in A· and is usually only *ca.* 5% of V_{rep} (due to the fact that this additional electron is rather far removed from the reaction centre). V_{rep}' is assumed[6] to be a Sato's function.

Equation (4) allows the calculation of activation energies, structures of activated states and (in conjunction with transition state theory) the evaluation of pre-exponential factors and kinetic isotope effects for reaction (1) in the gas phase. Unfortunately, the knowledge of rate parameters is at present so limited, that a full comparison with experiment is not possible. Moreover, most of the experimental results correspond to studies in solution, rather than in the gas phase. If we assume that the ratio of rate constants is independent of phase, and that pre-exponential factors for similar substrates are proportional to the number of hydrogen atoms available for reaction, then, equation (5) is valid. Equation (5) has been applied to aliphatic substrates (see Table) and quantitative agreement is obtained.

$$\frac{k_1}{k_2} = \frac{\exp(-Ea_1/RT)\ (no.\ H)_1}{\exp(-Ea_2/RT)\ (no.\ H)_2} \quad (5)$$

The results suggest that the biradical model is a good representation of a carbonyl triplet. The similarities with alkoxy radicals are due not only to electronic structure parallels, but to the similarity in reaction paths. The selectivity of different ketones are dependent mainly on the difference, $E_t - E_d$.

For agreement between the experimental and calculated absolute rate constants for the data in the Table a pre-

TABLE

Comparison of experimental and calculated relative rate constants at ca. 25° *using equation* (5)

Ketone	Substrate$_1$	Substrate$_2$	Exp. log (k_1/k_2)	Calc. log (k_1/k_2)
Benzophenone[a,b]	Cyclohexane	t-butylbenzene	1·19	1·65
Benzophenone[c]	cyclohexane	2,3-dimethylbutane	0·04	−0·22
Benzophenone[c]	cyclohexane	isopropyl alcohol	−0·64	−0·72
Benzophenone[c]	cyclohexane	2-octanol	−0·67	−0·72
Benzophenone[c]	isopropyl alcohol	2,3-dimethylbutane	0·69	0·94
Acetophenone[d,b]	cyclohexane	t-butylbenzene	1·16	1·09
Acetone[e,f]	isopropyl alcohol	n-butanol	−0·05	0·09
Butyrophenone[g,b]	cyclohexane	t-butylbenzene	1·14	0·96

[a] E_t = 68·7 kcal mol^{-1}; [b] from ref. 1b; [c] from ref. 1a; [d] E_t = 73·6 kcal mol^{-1}; [e] E_t = 79·0 kcal mol^{-1}; [f] A. G. Davies, B. P. Roberts, and J. C. Scaiano, unpublished work, determined by kinetic e.s.r. spectroscopy; [g] E_t = 75·0 kcal mol^{-1}.

† This is only applicable to $n \rightarrow \pi^*$ triplets, which formally have seven electrons on singly bonded oxygen.

exponential factor of about 2×10^8 M^{-1} s^{-1} *per hydrogen* atom is required.

The main assumptions of the biradical model are (i) that the reacting triplets are in thermal equilibrium, (ii) that there is no change in multiplicity in going from reactants to products and (iii) that the process is *adiabatic*.

(*Received, July* 15*th*, 1971; *Com.* 1220.)

[1] C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, 1965, **87**, 3361; A. Padwa, *Tetrahedron Letters*, 1964, 3465.
[2] P. J. Wagner, *Accounts Chem. Res.*, 1971, **4**, 168.
[3] A. G. Davies, D. Griller, B. P. Roberts, and J. C. Scaiano, *Chem. Comm.*, 1971, 196.
[4] D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1964, 1425.
[5] W. R. Bergmark, B. Beckmann, and W. Lindenberger, *Tetrahedron Letters*, 1971, 2259.
[6] S. W. Mayer and L. Schieler, *J. Phys. Chem.*, 1968, **72**, 236, and references therein.
[7] S. Sato, *J. Chem. Phys.*, 1955, **23**, 592, 2465.
[8] H. S. Johnston, "Gas Phase Reaction Rate Theory", Ronald Press, New York, 1966.