BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3510—3514 (1972)

A Consideration of Orbital Interaction in the Reaction of $^1\Delta_g$ Molecular Oxygen with Ethylene Derivatives

Satoshi Inagaki, Shinichi Yamabe, Hiroshi Fujimoto, and Kenichi Fukui
Faculty of Engineering, Kyoto University, Kyoto

(Received March 27, 1972)

The stereochemical path of the reaction between the $^1\Delta_g$ oxygen molecule and ethylene was examined in terms of orbital interaction. The results here obtained suggest that a path *via* the perepoxide intermediate or *via* a perepoxide-like transition state should be carefully examined in discussing not only the steric path to dioxetane, but also the mechanism of hydroperoxide formation.

Extensive studies[1] of the reactions of the $^1\Delta_g$ oxygen molecule with olefinic bonds have revealed the existence of cycloaddition products (both $2+2$[2] and $4+2$ cycloadducts[3–5]), allylic hydroperoxides,[4,6] and fragmentation products — that is, carbonyl compounds. The fact that a single species, the singlet oxygen, gives both $2+2$[2a] and $4+2$[1] cycloadducts, with the configuration of olefin retained, provides us with an interesting problem to be examined from the viewpoint of molecular orbital symmetry. In addition, there are now heated controversies[1] regarding the mechanism of the reactions between the singlet oxygen and ethylene derivatives, especially concerning the existence of the perepoxide intermediate or the perepoxide-like transition state. Here, the following questions come to mind. Is the 1,2-cycloadduct, namely, dioxetane, formed as a primary product or as a rearranged compound of an initially-formed intermediate, perepoxide? Furthermore, does a concerted "ene" reaction occur in fact, or does an allylic hydroperoxide have any precursor? If any, what is the precursor?

In order to obtain some information about the detailed reaction path, Kearns,[1,7] using correlation diagrams, recently examined three different models for the concerted addition of the singlet oxygen to ethylene, IA, IIA, and IIIA, and suggested that IA and IIA are generally allowed, while IIIA is allowed only for the olefins with particularly low π ionization potentials. These results, obtained from the correlation diagrams, are not necessarily satisfactory in our attempt to ascertain the stereochemistry of the reaction paths, for there remains the important problem of whether dioxetane, previously detected,[2] is a primary product or a rearranged product of perepoxide. Hence, another discussion from a different standpoint, that of particular orbital interaction,[8] is worth being presented.

Choice of Models

In discussing the mechanisms of both dioxetane and allyic hydroperoxide formations, perepoxide has been

---

1) D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971).

2) a) P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, **92**, 3223 (1970); b) S. Mazur and C. S. Foote, *ibid.*, **92**, 3225 (1970).

3) K. Gollnick and G. O. Schenck, "1,4-Cycloaddition Reactions", J. Hamer, Ed., Academic Press, New York, 1967, p. 255.

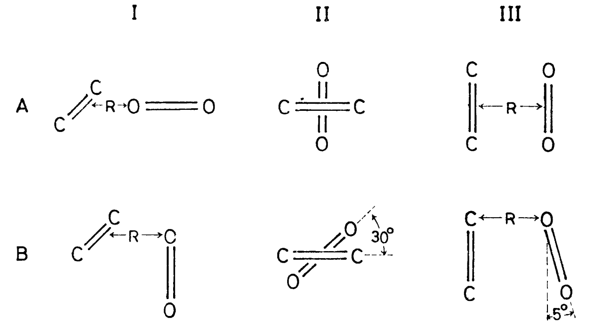
4) T. Matsuura, *Yūki Gōsei Kyōkai Shi*, **26**, 217 (1969).

5) Furthermore, a $6+2$ cycloadduct is proposed as the intermediate of the reaction of the singlet oxygen with cycloheptatriene. See, A. S, Kende and Y. -C. Chu, *Tetrahedron Lett.*, **1970**, 4937.

6) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1969).

7) D. R. Kearns, *J. Amer. Chem. Soc.*, **91**, 6554 (1969).

8) K. Fukui, *Accounts Chem. Res.*, **4**, 57 (1969) and the references cited therein.



recommended as a feasible intermediate,[1] but this recommendation still remains without any theoretical are experimental conclusive evidence for or against it. As typical models of perepoxide, IA and IB are chosen in this study. In IA, one oxygen is placed in the plane determined by the carbons of ethylene and the other oxygen, while one oxygen is located vertically away from the coplane in IB. IB is our originally-chosen model.

On the other hand, some concerted processes, namely, the $2\pi_s+2\pi_a$ and $2\pi_s+2\pi_s$ cycloadditions represented by the models IIA and IIIA respectively, have naturally been proposed[1] in analogy to ethylene dimerization.[9] It should be noted that the frontier orbitals to interact with each other are orthogonal; therefore, the overlapping between them is zero in IIA. Hence, the IIB model in which the plane containing the C_2 axis and O–O bond axis and the one containing the C_2 axis and the C–C bond axis intersect with the 30° angle, was examined in order to evaluate the actual effectiveness of IIA.

The last model, IIIB, will be used to examine the possibility of an unsymmetrical ionic or biradical-like transition state. The deformation from the symmetrical structure was introduced by rotating the O–O bond in the plane by an arbitrary angle (5°).

Consideration of the Particular Orbital Interaction

From numerous instances of actual chemical reactions, it is now well-established that a majority of chemical reactions take place at the position, and in the direction, where the overlapping between the highest occupied (HO) molecular orbital (MO) and the lowest unoccupied (LU) MO is most favored.[8] Accordingly, it is first necessary to look into the nodal properties of the frontier orbitals of $^1\Delta_g$ oxygen in order to determine the most probable reaction path in terms of particular orbital interaction.

The electronic configuration of $^1\Delta_g$ molecular oxygen is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2(1\pi_{gyz})^2(1\pi_{gzx})^0$ taking the O–O axis along the Z-axis. The MO's π_{gyz} and π_{gzx} have two nodal planes, one involving the O–O axis and the other perpendicular to this axis (Fig. 1). It follows that the singlet oxygen has the HOMO and the LUMO of the same symmetry property, extending in two planes perpendicular to each other.

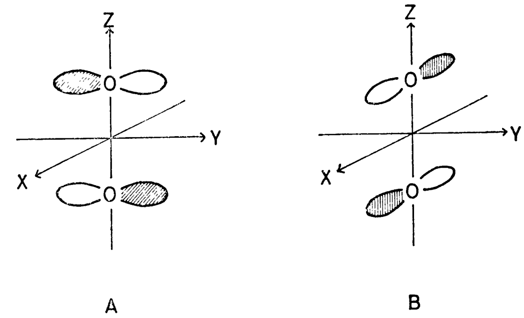


Fig. 1. The nodal property and the direction of the extension of the HOMO (A) and the LUMO (B) of $^1\Delta_g$ molecular oxygen.

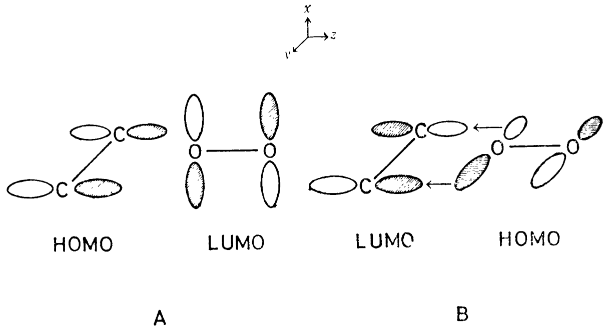


Fig. 2. The modes of HOMO-LUMO interactions between $^1\Delta_g$ molecular oxygen and ethylene in the model IA;
(A) intreraction between the HOMO of ethylene and the LUMO of $^1\Delta_g$ molecular oxygen;
(B) interaction between the LUMO of the former and the HOMO of the latter.

The IA model will first be considered here in terms of orbital interaction, which has been examined by means of a correlation diagram and which has been shown to represent an allowed process from the viewpoint of the conservation of orbital symmetry.[1] Suppose that the molecular plane and the C–C bond axis of ethylene are fixed parallel to the XY-plane and the Y-axis respectively, and $^1\Delta_g$ molecular oxygen is on the Z-axis (Fig. 2). Then, it can readily be found from the requirement of orbital symmetry that the HOMO of ethylene and the LUMO of the oxygen do not overlap at all, irrespective of any rotation of oxygen about the Z-axis (Fig. 2A). On the other hand, the LUMO of ethylene can overlap with the HOMO of the singlet oxygen because they have the same symmetry property with respect to reflection in the ZX-plane (Fig. 2B). This mode of orbital interaction may, however, be less important, since it means a charge-transfer from oxygen to ethylene; this mode of electron delocalization contradicts the generally-accepted electronegativity order. Accordingly, the model IA is not expected to represent the most favorable reaction path.

In the model IB, both modes of frontier orbital interactions which imply the charge-transfer from ethylene to oxygen, and the reverse, are favorable. The HOMO of ethylene can effectively interact with the terminus of the LUMO of the singlet oxygen (Fig. 3A), while the HOMO of oxygen, with its maxi-

---

[9] R. B. Woodward and R. Hoffmann, *Angew, Chem., Int. Ed. Engl.*, **8**, 781 (1969).

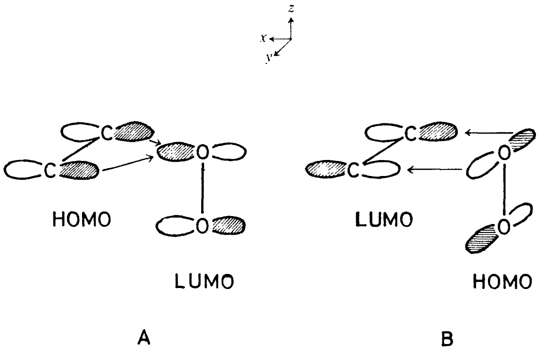


Fig. 3. The modes of HOMO-LUMO interactions between $^1\Delta_g$ molecular oxygen and ethylene in the model IB;
(A) interaction between the HOMO of ethylene and the LUMO of $^1\Delta_g$ molecular oxygen;
(B) interaction between the LUMO of the former and the HOMO of the latter.

mum extension in the direction parallel to the C–C bond, can also interact with the LUMO of ethylene (Fig. 3B), because these interacting MO's have the same symmetry with respect to the bisecting plane of the combined system (*ZX*-plane). Accordingly, the model IB may be supposed to be the most promising candidate for the actual reacting system.

A concerted mechanism can be alternative interpretation of the formation of 1,2-cycloadduct dioxetane. The characteristic of such a reaction path is that the way of approach of oxygen to ethylene maintains a certain symmetry, at lowest, the C_2 element. In these cases, there are two typical modes of frontier orbital interaction. One of them is a suprafacial-antarafacial interaction between the HOMO of the ethylenic π orbital and the LUMO of the singlet oxygen $1\pi_{gzx}$, as is illustrated in Fig. 4A (ethylene approaches oxygen along the *Y*-axis, with the π orbital in the *XY*-plane). This interaction mode, which corresponds to the IIA or IIB model, would not be so favored by the geometry as to eventuate in the stabilizing of the transition state. The other significant interaction is a suprafacial-suprafacial interaction between the LUMO of ethylene and the HOMO of the singlet oxygen (Fig. 4B, model IIIA). This mode of interaction is geometrically most feasible, but again it results in an unfavorable charge-transfer from the singlet oxygen to ethylene.

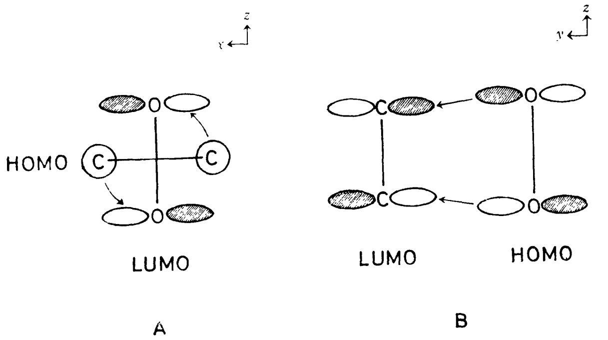


Fig. 4. The modes of HOMO-LUMO interactions between $^1\Delta_g$ molecular oxygen and ethylene in the model IIA and IIIA; (A) the interaction between the HOMO of ethylene (suprafacial) and the LUMO of the singlet oxygen (antarafacial) and (B) that between the LUMO of the former (suprafacial) and the HOMO of the latter (suprafacial).

The last model, IIIA, cannot be discussed here by taking only the orbital symmetry into consideration, for this model does not have any particular symmetry. Accordingly, the estimation of the IIIB model will be made by the MO calculation to be described in the following section.

As a result, $^1\Delta_g$ molecular oxygen is expected to approach a double bond of olefins, most probably forming trigonal ring composed of two carbons and an oxygen atom, and tailed by the other oxygen, which drops out of the plane of the ring.

Calculation

The chemical interaction at the early stage of a reaction was discussed by dividing the interaction energy, ΔW, into Coulomb (E_Q), exchange (E_K), delocalization (D), and polarization (Π) terms by the use of the configuration-interaction method (Eq. (1)):[10]

$$\Delta W = E_Q + E_K - D - \Pi. \tag{1}$$

E_Q is the quantity which reflects the charge distribution of the two independent reactants. E_K has a positive value with regard to the reactions between two closed-shell molecules, serving as a repulsive term. D is the stabilization energy due to the mixing-in of the charge-transferred states, in which one electron of an occupied MO of one molecule is transferred into an unoccupied MO of the other molecule. The last term, Π, contributes to the stabilization resulting from the involvement of the local excited states within one molecule under the influence of the approach of the other. The most preferable reaction path may be defined as the one which makes ΔW the smallest.

In Table 1, the results of the calculation are given with regard to some assumed models of the reaction of the singlet oxygen with ethylene derivatives. By comparing the terms in Table 1, we can see, first, that E_Q is zero, for the singlet oxygen has no net charge on both nuclei and Π is also small. The superiority or the inferiority of an assumed reaction path to others is determined essentially by the terms E_K and D. That is, the reaction may favorably proceed through a geometry capable of enlarging the D term and of depressing the E_K term. Accordingly, IA and IB can be expected to be more favorable than others. It is, however, noteworthy that the model IIIB has a re-

TABLE 1. INTERACTION ENERGIES BETWEEN $^1\Delta_g$ OXYGEN MOLECULE AND ETHYLENE, SHOWN IN eV.

	IA	IB	IIA	IIB	IIIA	IIIB
E_Q	0.000	0.000	0.000	0.000	0.000	0.000
E_K	0.110	0.158	0.186	0.213	0.221	0.182
D	0.058	0.082	0.019	0.033	0.041	0.033
Π	0.002	0.001	0.000	0.000	0.000	0.000
ΔW	0.051	0.075	0.167	0.181	0.180	0.148

---

[10] K. Fukui and H. Fujimoto, This Bulletin, **41**, 1989 (1968).

TABLE 2. THE ABSOLUTE VALUES OF INTERMOLECULAR OVERLAP INTEGRALS

Model IB

Oxygen	Ethylene					
	σ_2	σ_3	σ_4	σ_5	π	π^*
$2\sigma_g$	0	0.005	0.004	0	0.017	0
$2\sigma_u$	0	0.006	0.001	0	0.007	0
$1\pi_u$	0	0.005	0.002	0	0.020	0
$1\pi_u$	0.006	0	0	0.002	0	0.007
$3\sigma_g$	0	0.002	0.001	0	0.002	0
$1\pi_g$	0.001	0	0	0.002	0	0.003
$1\pi_g$	0	0.006	0.001	0	0.008	0
$3\sigma_u$	0	0.002	0.000	0	0.001	0

Model IIIA

Oxygen	Ethylene					
	σ_2	σ_3	σ_4	σ_5	π	π^*
$2\sigma_g$	0	0	0.005	0	0.020	0
$2\sigma_u$	0.010	0	0	0	0	0.012
$1\pi_u$	0	0.006	0	0	0	0
$1\pi_u$	0	0	0.003	0	0.025	0
$3\sigma_g$	0.000	0	0.004	0	0.003	0
$1\pi_g$	0.010	0	0	0	0	0.014
$1\pi_g$	0	0	0	0.003	0	0
$3\sigma_u$	0.002	0	0	0	0	0.001

latively low ΔW, implying a tendency toward a biradical-like character of the reactions.

In order to examine E_K and D in detail, it is worthwhile to look into the overlap integrals between the MO's of oxygen and ethylene (given in Table 2), since both the energy terms, E_K and D, are overlap-dependent quantities. Roughly speaking, E_K is parallel to the overlap integrals between the occupied MO's of oxygen and the occupied MO's of ethylene, while D increases as the magnitueds of the overlap integrals increase between the occupied MO's and the unoccupied MO's of the two species. With this as well as the orbital symmetry in mind, we will compare the values of the overlaps, especially with regard to two different models, IB and IIIA.

Among the overlaps, some larger values are found, in which the HOMO, denoted by π, of ethylene, participates. This π orbital, having a large extension in the direction of the singlet oxygen, can overlap with the MO's of the oxygen with a suitable symmetry property, that is, σ_g and π_u in the model IIIA, and all the MO's in the model IB except for $1\pi_u$ and $1\pi_g$ having an extension of the lobes perpendicular to the π orbital of ethylene. The overlap integrals between the π MO of ethylene and $2\sigma_u$, $1\pi_u$, and $3\sigma_g$ of the singlet oxygen in the model IIIA are larger than the corresponding ones in the model IB. This presumably results from the difference in the geometry of the assumed models. In the model IIIA, the relevant orbital lobes extend face to face with each other, while, in the model IB, only a terminus of singlet oxygen can be effectively involved in the orbital overlapping. It follows that, though the π of ethylene can overlap with more MO's of the singlet oxygen in IB than in IIIA, the absolute values are smaller. In addition, since, in the model IIIA, there are considerably large overlap integrals between σ_2 of ethylene and the σ_u and π_g of the singlet oxygen, as well as the accumulating contributions of the other modes of exchange interaction, a larger value of E_K results in IIIA compared with that in the IB model. The sum of the squares of the overlap integrals between the occupied MO's of ethylene and the occupied MO's of the singlet oxygen was calculated to be 1.31×10^{-3} in the model IB and 1.84×10^{-3} in the model IIIA. Therefore, the preference of the model IB to the model IIIA is partly attributable to the smaller occupied-occupied MO interactions, resulting in the smaller exchange energy E_K.

Table 2 gives other valuable information about the orbital interaction between the occupied MO's of one molecule and the unoccupied MO's of the other, that interaction contributing to the stabilization of the system through the delocalization energy, D. That the overlap integral is zero between the LUMO $1\pi_g$ of the singlet oxygen and the HOMO π of ethylene in the IIIA model indicates numerically that this orbital interaction is symmetry-forbidden, as has been described in the previous section of considering orbital interaction. On the other hand, the orbital interaction between the LUMO of ethylene and the HOMO of oxygen is symmetry-allowed. In the model IB, both the HOMO–LUMO interactions are allowed. Although the overlap integral between ethylene π^* and oxygen π_g is a larger value, 0.014, in the model IIIA as compared with the others, this charge-transfer state is located too high (~9.4 eV) above the initial state. Therefore, this interaction does not contribute very effectively to the stabilization of the reacting system, since the delocalization energy is in inverse proportion to the energy difference. On the contrary, the interaction between the HOMO of ethylene and the LUMO of oxygen is favorable because of the smaller energy difference between this charge-transfer state and the initial state (2.6 eV). As a result, in spite of the smaller value of the overlap integral in the model IB (0.008), this HOMO–LUMO interaction, in which ethylene acts as an electron-donor and the oxygen serves as an electron-acceptor, yields a larger stabilization in the model IB than the HOMO–LUMO interaction in the model IIIA as mentioned above. Thus, the examination of the exchange and delocalization energies in terms of MO overlap integrals reveals the reason for the superiority or inferiority of one assumed reaction path to another.

The HOMO–LUMO interaction reflected by the D term is now found to be most favored in the geometry of the model IB among all the models examined here. On the contrary, the smaller value of E_K for the model IA than for IB reserves the possibility of the preference of IA. Any attempt to reach a conclusive statement about the preference of IA or of IB is futile, since it depends on the subtle balance between D and E_K terms. The most favorable geometry of the transition state can probably be expected

Table 3. Total energy evaluated by CNDO method

	IA	IB	IIA	IIB	IIIA	IIIB
R=2Å	−1451.874	−1451.897	−1450.977	−1450.939	−1450.912	−1451.237
R=3Å	−1452.769	−1452·760	−1452.748	−1452.749	−1452.748	−1452.755
Difference	0.895	0.863	1.771	1.810	1.836	1.518

to assume a nuclear configuration intermediate between IA and IB.

A CNDO[11] calculation was carried out with respect to the six models (IA, IB, IIA, IIB, IIIA, and IIIB) in order to affirm the conclusion drawn from the consideration and the calculation of orbital interaction. As the numerical values in Table 3 show, the nuclear configurations represented by the models IA and IB have lower total energies than the other, corresponding models.[12] In addition, these two models are less destabilized than the others as the two reactants approach further from R=3Å to R=2Å, as is shown in Table 3.[12] This result is in conformity with the prediction of the previous calculation of intermolecular interactions.

Conclusion

The speculative consideration of particular orbital interaction between the frontier orbitals supplies us with some information concerning the modes of interaction between $^1\Delta_g$ molecular oxygen and ethylene derivatives. The finding that the nuclear configuration represented by the model I is energetically favorable for the early-stage interaction between $^1\Delta_g$ molecular oxygen and ethylene is interesting since the way of the approach of a diatomic molecule with the HOMO and the LUMO of the same symmetry to ethylene has now been examined for the first time.

Our present study seems to suggest the presence of a perepoxide intermediate (which may or may not be stable) on the route to the corresponding dioxetane,[14] which is then readily subjected to decomposition into carbonyl compounds.[16] It is also probable that a perepoxide intermediate may be rearranged to allylic hydroperoxide.[17] Alternatively, it is likely that the allylic hydroperoxides are formed through a perepoxide-like transition state.

It may be true that there is some room for reviewing the choices of the models, especially in connection with the intermolecular distances and the changes in the nuclear configurations with the progress of the reaction to be compared, but the essential features of the reactions of $^1\Delta_g$ molecular oxygen with ethylene derivatives, which are derived here from our considerations and from the calculation of the orbital interaction, could not be very much changed by choosing the assumed models. With all the features here revealed, we can say with some certainty that a suprafacial-antarafacial interaction, as in the case of thermal dimerization of ethylene derivatives, is directly inapplicable to the reaction path to dioxetane formation, and that a path *via* a perepoxide intermediate or a perepoxide-like transition state should be carefully examined in discussing not only the steric path to dioxetane, but also the mechanism of hydroperoxide formation.

---

[11] J. A. Pople and D. L. Beveridge, "Approximate Molecular Oribital Theory", McGraw-Hill Book Co., New York, 1970.

[12] The extended Hückel MO method[13] gives the same prediction.

[13] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

[14] The intermediate of the photosensitized oxidation of indene to the exclusive formation of homophthaldehyde in methylene chloride,[15] was trapped by menthanol and was reduced to *vicinal*-hydroxy-methoxy-2,3-dihydroindene.[15] This result suggests the intermediacy of dioxetane[15] or that of perepoxide. However, it should be noted that the possibilities of the photochemical reaction between the olefin and methanol and the reaction between $^1\Delta_g\mathrm{O}_2$ and methanol cannot be ruled out here.

[15] W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, **91**, 3396 (1969).

[16] K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969).

[17] Fenical *et al.*[18] proposed allylic hydroperoxides arise from perepoxide on the basis of the experimental results that the photooxydation of 1,2-dimethylcyclohexene yielding normal allylic hydroperepoxide affords *vicinal*-hydroxy-azido-derivative in the presence of azide ion. However, this proposal was recently pointed out to be irrelevant because of direct involvement of azide in azidohydroperoxide formation.[19]

[18] W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, **91**, 7771 (1969).

[19] C. S. Foote, T. T. Fujimoto, and Y. C. Chang, *Tetrahedron Lett.*, **1972**, 45; N. Hasty, P. B. Merkel, P. Radlick, and D. R. Kearns, *ibid.*, **1972**, 49.