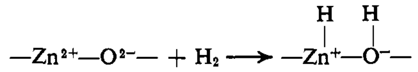
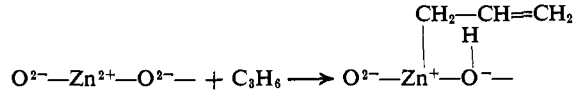
tensity of the OH band. Slight changes also occur in the C–H and C–D region of the spectra.

The above data clearly show that hydrogen is removed from propylene to form an allyl group. If, following Burwell's picture of adsorption on chromia,[5b] we view hydrogen adsorption on zinc oxide as heterolytic



$$-\mathrm{Zn}^{2+}-\mathrm{O}^{2-}- + \mathrm{H}_2 \longrightarrow -\overset{\mathrm{H}}{\overset{|}{\mathrm{Zn}^{+}}}-\overset{\mathrm{H}}{\overset{|}{\mathrm{O}^{-}}}-$$

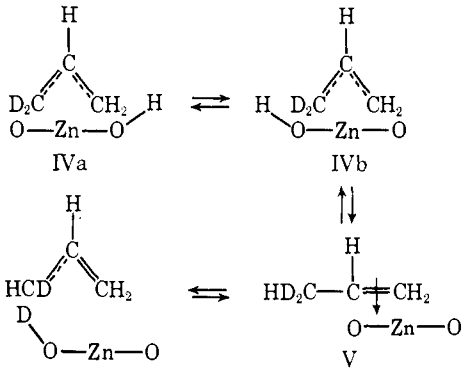
the formation of an allyl species involves a similar heterolytic fission



$$\mathrm{O}^{2-}-\mathrm{Zn}^{2+}-\mathrm{O}^{2-}- + \mathrm{C_3H_6} \longrightarrow \mathrm{O}^{2-}-\overset{\mathrm{CH_2-CH=CH_2}}{\overset{|}{\mathrm{Zn}^{+}}}-\overset{\mathrm{H}}{\overset{|}{\mathrm{O}^{-}}}-$$

III

Such a formulation has the advantage that it offers a natural explanation of why no ZnH band is observed: the allyl group blocks the Zn part of the active site. The shift in the C=C bond frequency suggests there is participation of the π bond in the bonding. When manganese carbonyl reacts with allyl chloride to form a σ-allyl complex (III), the double-bond frequency (1620 cm$^{-1}$)[11] is only slightly different from that for gaseous propylene (1652 cm$^{-1}$).[12] However, when it forms a π-allyl complex (IV), the double-bond frequency shifts dramatically, *i.e.*, to 1505 cm$^{-1}$.[11] Such behavior is typical of transition metal–allyl complexes. Since the shift in double-bond frequency we observe is pronounced, it seems reasonable to view the surface species as a π-allyl complex bound to zinc. With this interpretation, the changes with time that are found in the spectrum of adsorbed 1,1-dideuteriopropylene can be accommodated by the following.[13]



Three further points should be stressed. (1) In the above discussion we include the "dynamic" allyl system (which may be more than one type of species[14]) in the term π-allyl complex; the infrared spectra are not sufficiently diagnostic to differentiate these species.[15]

(2) The bonding to the surface zinc atom involves more π interaction than that found for diallylzinc in solution; for the latter $\nu_{\mathrm{C=C}}$ occurs at 1613 to 1622 cm$^{-1}$ [16] compared to 1545 cm$^{-1}$ for the adsorbed species.

(3) Propylene may form other species on the surface; our results indicate only that the π-allyl complex is the major (and perhaps the only) surface species present.

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The authors also thank R. L. Burwell, Jr., for making available unpublished results from his laboratory.[5b]

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[13] Consequences of such a sequence in the double-bond migration of higher olefins, catalyzed by metal complexes, have been discussed recently by J. F. Harrod and A. J. Chalk, *J. Amer. Chem. Soc.*, 88, 3491 (1966).

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[15] G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter, and H. Zimmerman, *Angew. Chem. Intern. Ed. Engl.*, 5, 151 (1966).

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**A. L. Dent, R. J. Kokes**
*Chemistry Department, The Johns Hopkins University*
*Baltimore, Maryland 21218*

*Received November 8, 1969*

## Self-Reaction of Diethylnitroxide Radicals[1]

*Sir:*

Although the self-reactions of alkylperoxy radicals have received considerable attention in recent years,[2–6] the self-reactions of the isoelectronic dialkylnitroxide radicals have been almost entirely neglected. We wish to report the results of an esr investigation of the self-reaction of diethylnitroxide carried out over a wide range of temperature. The results show some interesting parallels and differences when compared with the behavior of the alkylperoxy radicals.

The experimental procedure was similar to that employed in our studies of peroxy radicals.[5] The nitroxide was best prepared from $10^{-2}$ *M* diethylhydroxylamine in $\mathrm{CF_2Cl_2}$ by direct photolysis at temperatures below −60° and by photolysis in the presence of $10^{-1}$ *M* di-*t*-butyl peroxide above −60°. The spectrum was similar to that previously reported for diethylnitroxide formed in the reaction of diethylformamide with hydrogen peroxide.[7] The radicals generally disappeared with reasonably clean second-order kinetics, occasional deviations being observed at the beginning or end of the main decay. These deviations are presumably due to the formation of some radicals having stabilities different from that of the main radical, diethylnitroxide. The same bimolecular rate constant was obtained from decays measured over two orders of magnitude in the initial radical concentration.

The rate constant for the decay of tertiary peroxy radicals decreases rapidly as the temperature is lowered ($E_{\mathrm{t}}$ = 8–9 kcal/mol[2–6]). In complete contrast the temperature coefficient for the decay of diethylnitroxide in $\mathrm{CF_2Cl_2}$ is very small or zero.[8] At 30° the bimolecu-

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[1] Issued as NRCC No. 11223.

[2] K. U. Ingold, *Accounts Chem. Res.*, 2, 1 (1969).

[3] J. A. Howard and K. U. Ingold, *Can. J. Chem.*, 47, 3797 (1969).

[4] J. A. Howard, K. Adamic, and K. U. Ingold, *ibid.*, 47, 3793 (1969).

[5] K. Adamic, J. A. Howard, and K. U. Ingold, *Chem. Commun.*, 505 (1969); *Can. J. Chem.*, 47, 3803 (1969).

[6] J. E. Bennett, D. M. Brown, and B. Mile, *Chem. Commun.*, 504 (1969); *Trans. Faraday Soc.*, in press.

[7] A. Hudson and H. A. Hussein, *J. Chem. Soc., B*, 1299 (1967).

[8] This is also true of diethylnitroxide in benzene from 7 to 70° and in isopentane from 30 to −60°.

lar rate constant, $k_{\mathrm{esr}}$, is $(1.2 \pm 0.2) \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$.[9] At $-135°$, $k_{\mathrm{esr}}$ is $(3 \pm 1) \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$. The results over the entire temperature range give $k_{\mathrm{esr}} = 10^{(5\pm1)} \exp[(-1000 \pm 500)/RT]\ M^{-1}\ \mathrm{sec}^{-1}$.

Tertiary peroxy radicals exist in a reversible equilibrium with dimeric tetroxide below $\sim -90°$. Dialkylnitroxides have never been reported to form dimers[10] and, in fact, we have used 2,2,6,6-tetramethylpiperidonenitroxide to calibrate radical concentrations at temperatures as low as $-160°$ without seeing any evidence for dimer formation. However, perhaps because of decreased steric hindrance, diethylnitroxide does form a dimer in $CF_2Cl_2$ (and also in isopentane). The dimer was identified by the fact that the nitroxide concentration could be increased and decreased by raising and lowering the temperature in the range $-100$ to $-145°$. Because the irreversible decomposition of the nitroxide is quite rapid even at these low temperatures it is not possible to form very much of the dimer–nitroxide equilibrium mixture. That is, high concentrations of nitroxide decrease by irreversible decay up to the point where this rate is small compared with the length of an experiment. It is this "residual" nitroxide concentration, maximum $\sim 2 \times 10^{-6}\ M$, which is in equilibrium with a "residual" concentration of dimer (eq 1). The

$$2(CH_3CH_2)_2NO\cdot \rightleftharpoons \{(CH_3CH_2)_2NO\}_2 \qquad (1)$$

equilibrium constant is given by

$$K_1 = \frac{k_{-1}}{k_1} = \frac{[(CH_3CH_2)_2NO\cdot]^2}{[\{(CH_3CH_2)_2NO\}_2]} = \frac{2[(CH_3CH_2)_2NO\cdot]^2}{[(CH_3CH_2)_2NO\cdot]_{\max} - [(CH_3CH_2)_2NO\cdot]}$$

where $[(CH_3CH_2)_2NO\cdot]_{\max}$ is the radical concentration at complete dissociation. The variation in the equilibrium constant with temperature can be represented by the van't Hoff relation

$$K_1 = e^{\Delta S_1/R} e^{-\Delta H_1/RT}$$

where $\Delta S$ is the change in entropy and $\Delta H$ the change in enthalpy. The variation in the nitroxide concentration with temperature gave $\Delta H = 8.5 \pm 0.5$ kcal/mol and $\Delta S = 32 \pm 4$ gibbs/mol at 1 mol/l. standard state. These values are remarkably similar to those we found previously for the tertiary peroxy radical–tetroxide equilibria, *viz.*,[5] $\Delta H = 9.0$ kcal/mol, $\Delta S = 33$ gibbs/mol.[13]

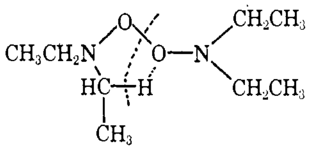
Although our data could be interpreted by a reaction scheme in which the dimer has no direct bearing on the overall reaction, *i.e.*

$$\{(CH_3CH_2)_2NO\}_2 \underset{-1}{\overset{1}{\rightleftharpoons}} 2(CH_3CH_2)_2NO\cdot \xrightarrow{2} (CH_3CH_2)_2NOH + CH_3CH{=}N(O)CH_2CH_3$$

it is difficult to believe that reaction 2, a hydrogen atom abstraction, could occur almost without activation energy and with a preexponential factor as low as $10^5$ (*cf.* ref 14). We therefore prefer to represent the reaction as

$$2(CH_3CH_2)_2NO\cdot \underset{-1}{\overset{1}{\rightleftharpoons}} \{(CH_3CH_2)_2NO\}_2 \xrightarrow{3} (CH_3CH_2)_2NOH + CH_3CH{=}N(O)CH_2CH_3$$

with the measured decay rate constant $k_{\mathrm{esr}} = k_3/K_1$, from which we obtain $k_3 = 10^{12} \exp(-9500/RT)\ \mathrm{sec}^{-1}$. The preexponential factor for reaction 3 is within the range generally found for unimolecular decompositions proceeding by five- or six-center cyclic transition states.[14] Assuming the dimer is formed by head-to-head coupling of the nitroxide radicals[15] the transition state might be represented as



The measured entropy change accompanying step 1 is 32 gibbs/mol. The entropy loss accompanying the formation of the cyclic transition state will be that due to the loss from three hindered internal rotors at $-3.6$ gibbs/mol per rotor[14,16] plus a symmetry contribution of $R \ln 8$ since any of eight equivalent hydrogens may be transferred. That is, $\Delta S_3^{\ddagger} = 3(-3.6) + R \ln 8 = -10.8 + 4.2 = -6.6$ gibbs/mol. The preexponential factor for the overall decay can be estimated as $A_{\mathrm{esr}} = (ekT/h)(10^{-6.6/2.3R}/10^{32/2.3R}) = 10^{4.6}\ M^{-1}\ \mathrm{sec}^{-1}$ at the mean temperature of the experiments (220°K). This value is in gratifying agreement with the value found by direct measurement.

In conclusion, the present results indicate that diethylnitroxide radicals react reversibly with one another to form a dimer which can decompose *via* a cyclic transition state. The overall process is closely analogous to that proposed by Russell for secondary peroxy radicals.[17]

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[9] The room-temperature rate constant decreases by almost two orders of magnitude with increasing solvent polarity along the series isopentane > benzene > $CF_2Cl_2$ > methanol > $H_2O$. The N and H splittings increase along this series.

[10] Potassium nitrosodisulfonate ($(KSO_3)_2NO$, Fremy salt) is diamagnetic in the solid state[11] and bis(trifluoromethyl)nitroxide ($(CF_3)_2NO\cdot$) gives a diamagnetic solid at $-160°$.[12]

[11] A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, p 192.

[12] Reference 11, p 199.

[13] The calculated entropy change for this equilibria at 150°K is 30.4 gibbs/mol at 1 mol/l. standard state (S. W. Benson, private communication).

[14] S. W. Benson, "Thermochemical Kinetics," John Wiley & Sons, Inc., New York, N. Y., 1968.

[15] An analogous five-center structure can be drawn for $Et_2N(O)$-$N(O)Et_2$ and either a four- or six-center structure for $Et_2NON(O)Et_2$.

[16] H. E. O'Neal and S. W. Benson, private communication.

[17] G. A. Russell, *J. Amer. Chem. Soc.*, **79**, 3871 (1957).

**K. Adamic, D. F. Bowman, K. U. Ingold**
*Division of Chemistry*
*National Research Council of Canada, Ottawa, Canada*

*Received November 12, 1969*

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## Free Radical Epimerization at Unactivated Tertiary Carbon Atoms in Cyclohexane Derivatives

*Sir:*

We have recently reported[1] a new method for epimerization at unactivated tertiary carbon atoms in saturated cyclopentane derivatives by irradiation in the presence of mercuric bromide or N-bromosuccinimide in hydrocarbon solution. We have now extended this method to unactivated teritary carbon atoms in saturated cyclohexane systems.

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[1] M. Gorodetsky and Y. Mazur, *J. Amer. Chem. Soc.*, **90**, 6540 (1968).