therefore do not yield singlet oxygen in significant quantities.

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Rate Constants for the Self-Reactions of *n*- and *sec*-Butylperoxy Radicals and Cyclohexylperoxy Radicals. The Deuterium Isotope Effect in the Termination of Secondary Peroxy Radicals[1,2]

Sir:

It is a requirement of the Russell cyclic mechanism[3] for the self-reaction of secondary peroxy radicals that the α hydrogen on one peroxy radical is transferred to the second peroxy radical in one of the rate-controlling steps of the reaction.[4] The rate of reaction should therefore be lower the more firmly the α hydrogen is bound to the peroxy radical. Furthermore, the reaction should exhibit a deuterium isotope effect if the α hydrogen is replaced by deuterium.[3,5] We have now definitely observed both effects.

The α hydrogen will be more firmly bound in a peroxy radical derived from a saturated hydrocarbon than in one in which the peroxy group is adjacent to a π-electron system. We have measured absolute termination constants at 30° for many peroxy radicals of the latter type[6] since the parent hydrocarbons are readily oxidized. Although it is not possible to obtain a reasonable chain length by oxidizing unbranched paraffins at 30°, the termination constants for saturated peroxy radicals can be readily obtained by the following procedure. A saturated hydroperoxide, R'OOH, is added to a readily oxidizable substrate, RH, in sufficient quantity that all the peroxy radicals involved in hydrogen abstraction from RH and involved in termination are derived from the added hydroperoxide.[7] The reaction scheme can be represented as

Initiation

$$\longrightarrow \mathrm{R}\cdot \qquad (1)$$

Propagation

$$\mathrm{R}\cdot + \mathrm{O_2} \longrightarrow \mathrm{ROO}\cdot \qquad (2)$$

(transfer)

$$\mathrm{ROO}\cdot + \mathrm{R'OOH} \longrightarrow \mathrm{ROOH} + \mathrm{R'OO}\cdot \qquad (3)$$

$$\mathrm{R'OO}\cdot + \mathrm{RH} \longrightarrow \mathrm{R'OOH} + \mathrm{R}\cdot \qquad (4)$$

Termination

$$\mathrm{R'OO}\cdot + \mathrm{R'OO}\cdot \longrightarrow \text{inactive products} \qquad (5)$$

Rate constants for the self-reaction of saturated peroxy radicals derived from *n*- and *sec*-butyl hydroperoxide and cyclohexyl hydroperoxide[8] were obtained by the rotating sector method using tetralin and α-methylstyrene as the oxidation substrates. These results are compared in Table I with previously determined[6] rate constants for chain termination in oxidizing hydrocarbons which give peroxy radicals of generally similar structure except that the α hydrogen is activated by a π-electron system. In all three cases the rate constants for the self-reactions of the saturated peroxy radicals are significantly smaller than for the unsaturated radicals.

Table I. Comparison of Termination Constants ($2k_5$ in M^{-1} sec^{-1}) for Saturated and Unsaturated Peroxy Radicals at 30°

Saturated peroxy radical from	Unsaturated peroxy radical from
n-Butyl hydroperoxide (0.4×10^8)	1,4-Pentadiene (11×10^8)
sec-Butyl hydroperoxide (1.5×10^6)	3-Heptene (6.4×10^6)
Cyclohexyl hydroperoxide (2.0×10^6)	Cyclohexene (5.6×10^6)

Previous work[3,5] has suggested that replacement of the α hydrogen by deuterium reduces the rate constant for the chain termination of secondary peroxy radicals by about a factor of 2. Because of the uncertainties involved in the initial experiments, we have remeasured this isotope effect by a more sensitive procedure. Diphenylmethyl hydroperoxide and *sec*-butyl hydroperoxide (normal, or deuterated at the α position[9]) were added to an oxidizable substrate as already described. Under standard conditions, differences in the oxidation rates in the presence of normal and deuterio hydroperoxide must reflect differences in the rate constant of reaction 5 (*i.e.*, in the rate constant of termination) since all the other rate constants will be identical. The results are given in Table II. The average isotope effect, $(k_5)_\mathrm{H}/(k_5)_\mathrm{D} = 1.37 \pm 0.14$, confirms the earlier work. The α hydrogen must be transferred in the rate-determining step of chain termination.

Table II. Deuterium Isotope Effect in Chain Termination at 30°

Peroxy radical	Substrate	$(\mathrm{Rate})_\mathrm{H}/(\mathrm{rate})_\mathrm{D}$
$\mathrm{Ph_2CH(D)OO}\cdot$	Tetralin	1.21
$\mathrm{Ph_2CH(D)OO}\cdot$	Styrene	1.37
$\mathrm{Ph_2CH(D)OO}\cdot$	Diphenylmethane	1.51
$\mathrm{C_2H_5(CH_3)CH(D)OO}\cdot$	Tetralin	1.23
$\mathrm{C_2H_5(CH_3)CH(D)OO}\cdot$	Styrene	1.51

The present results taken together with the fact that singlet oxygen is evolved in the self-reaction of *sec*-butylperoxy radicals[4] provide convincing evidence that the Russell mechanism plays an important role in the termination of oxidation chains involving secondary

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[1] Absolute Rate Constants for Hydrocarbon Oxidation. X. For part IX see J. A. Howard and K. U. Ingold, *J. Am. Chem. Soc.*, **90**, 1056 (1968).

[2] Issued as N.R.C. No. 9993.

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

[4] The transition state is represented in the preceding communication.[1]

[5] J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **43**, 2737 (1965), **44**, 1119 (1966).

[6] J. A. Howard and K. U. Ingold, *ibid.*, **45**, 793 (1967).

[7] J. A. Howard, W. J. Schwalm, and K. U. Ingold, Preprints of the International Oxidation Symposium, Vol. 1, Stanford Research Institute, San Francisco, Calif., 1967, p 3.

[8] A sample of which was kindly provided by R. C. Williamson, Jr., of Gulf Research and Development Co.

[9] The α-deuterio alcohols were prepared from the ketones by reduction with lithium aluminum deuteride and were then converted to the α-deuterio hydroperoxides by known methods.[10,11] The normal hydroperoxides were also prepared from the ketones by the same procedures.

[10] A. G. Davies, R. V. Foster, and A. M. White, *J. Chem. Soc.*, 1541 (1953).

[11] H. R. Williams and H. S. Mosher, *J. Am. Chem. Soc.*, **76**, 2987 (1954).

(and primary) peroxy radicals at room temperature. The relative importance of the alternate mode of reaction, formation of oxygen and two alkoxy radicals which rapidly disproportionate, has still to be determined. It is to be expected that the importance of this reaction mode will depend on the peroxy radical and will increase with increasing temperature.[12] It is perhaps worth pointing out that even exclusive termination by the Russell mechanism does not imply that all peroxy radical self-reactions are chain terminating. The electronically excited ketone (n,π*) occasionally formed in the termination process[13] is an active hydrogen atom abstracting species[14] quite capable of continuing the chain. However, the efficiency of excitation of the ketone appears to be too low ($\sim10^{-5}$–10^{-6})[13] to account for the reported 10% excess of cyclohexanol over cyclohexanone found in the products of pulse-radiolyzed cyclohexane saturated with oxygen.[15]

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[12] The activation energy for this type of decomposition of tertiary tetroxides is as high as 11–14.5 kcal/mole: P. D. Bartlett and G. Guaraldi, *J. Am. Chem. Soc.*, **89**, 4799(1967); J. R. Thomas and K. U. Ingold, Preprints of the International Oxidation Symposium, Vol. 1, Stanford Research Institute, San Francisco, Calif., 1967, p 517.

[13] R. F. Vasil'ev, *Progr. Reaction Kinetics*, **4**, 305 (1967).

[14] Comparable to a *t*-butoxy radical. See, *e.g.*, C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **87**, 3361 (1965).

[15] A. Maclachlan, *ibid.*, **87**, 960 (1965); R. Blackburn and A. Charlesby, *Trans. Faraday Soc.*, **62**, 1159 (1966); W. A. Cramer, *J. Phys. Chem.*, 71, 1171 (1967); *cf.* however, 71, 1112 (1967).

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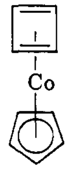
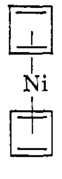
Cyclobutadiene(π-cyclopentadienyl)cobalt

Sir:

The effective atomic number rule provides a useful though not infallible guideline when attempting to predict novel organometallic systems which might possess thermodynamic stability. Thus dibenzenechromium, benzene(π-cyclopentadienyl)manganese, and bis(cyclopentadienyl)iron (ferrocene) all conform to this rule. Extension of this particular series to cobalt and nickel suggests that cyclobutadiene(π-cyclopentadienyl)cobalt (I) and bis(cyclobutadiene)nickel (II) might also exist as stable sandwich complexes.

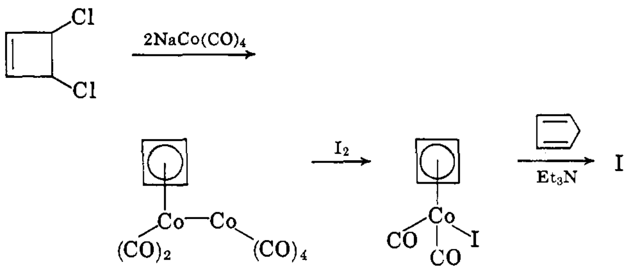


I



II

The tetraphenylcyclobutadiene analog of I and, more recently, the tetramethylcyclobutadiene derivative have been reported.[1,2] We now wish to report the isolation of the parent system I. The key step in the synthesis, the formation of the cyclobutadiene–cobalt bond, employs the reaction between 3,4-dichlorocyclobutene and a metal carbonyl anion; such interactions have recently been found useful for the preparation of other novel cyclobutadiene–metal complexes.[3]



III IV

Treatment of 3,4-dichlorocyclobutene with 2 moles[4] of $NaCo(CO)_4$ in tetrahydrofuran produced cyclobutadienedicobalt hexacarbonyl (III) [bright red crystals from pentane,[5] mp 38°; nmr, τ 5.42 (singlet)]. Reaction of complex III with iodine gave cyclobutadienecobalt dicarbonyl iodide (IV) [red crystals, mp 85° dec; nmr, τ 5.32 (singlet)]. Treatment of the iodide IV with cyclopentadiene and triethylamine in refluxing tetrahydrofuran produced cyclobutadiene(π-cyclopentadienyl)cobalt together with π-cyclopentadienylcobalt dicarbonyl which were separated by chromatography.

Cyclobutadiene(π-cyclopentadienyl)cobalt forms yellow crystals from pentane, mp 83–85°. The nmr spectrum of the compound consists of two sharp singlets at τ 5.14 and 6.39 having areas of 5:4, respectively. The mass spectral cracking pattern shows, among others, prominent peaks at 176 (56%), 150 (28%), and 124 (100%) corresponding to the parent molecular ion and the ions following loss of C_2H_2 and C_4H_4 fragments, respectively. When kept under nitrogen the compound is stable, but in air it appears to undergo very slow oxidative decomposition.

In view of the extensive substitution reactions known to occur on the ligand rings in ferrocene, the question as to whether similar aromatic character would be exhibited by the complex I is of interest. Furthermore, since the cyclobutadiene ligand in the complex cyclobutadieneiron tricarbonyl readily participates in electrophilic substitution reactions[6] and, as Rausch and Genetti have recently shown, the cyclopentadienyl ring in tetraphenylcyclobutadiene(π-cyclopentadienyl)cobalt can also be substituted,[7] then the question as to the relative reactivity of the two rings in I is an additional point of interest.

Initial results indicate that electrophilic substitution reactions do occur with the complex I and that the cyclobutadiene ring is much more reactive in this respect than the cyclopentadienyl ring. Treatment of I with acetyl chloride and aluminum chloride affords the acetyl derivative V; however, under the conditions used[8] extensive decomposition occurred and the yield of V was poor (*ca.* 10%). The acetyl derivative showed nmr absorptions at τ 5.13, 5.72, 6.15, and 8.12 having areas of 5:2:1:3, respectively. Acetoxymercuration with $Hg(OAc)_2$ in acetic acid produces the acetoxy-

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[1] A. Nakamura and H. Hagihara, *Bull. Chem. Soc. Japan*, **34**, 452 (1961).

[2] R. Bruce and P. M. Maitlis, *Can. J. Chem.*, **45**, 2017 (1967).

[3] R. G. Amiet, P. C. Reeves, and R. Pettit, *Chem. Commun.*, in press.

[4] An early product in reaction is cyclobutadienecobalt dicarbonyl chloride which appears to react rapidly with $NaCo(CO)_4$ to produce III; hence, 2 moles of $NaCo(CO)_4$ is used.

[5] The elemental analysis of this material and the other new compounds reported in this paper were in satisfactory agreement with expected values.

[6] J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 3254 (1965).

[7] M. D. Rausch and R. A. Genetti, *ibid.*, **89**, 5502 (1967).

[8] Under the same conditions cyclobutadieneiron tricarbonyl affords the acetyl derivative in 95% yield.