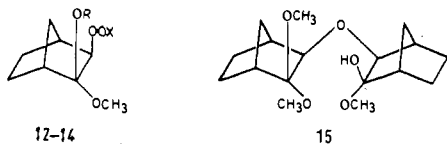corporating solvent appeared (Table I).

The hydroperoxides **12** and **13** were easily identified by their reduction with triphenylphosphine to the ketal alcohols **10** and **9**, respectively.[11]

12–14   15

The effect of solvent is dramatic. The reaction is much slower in methanol than in its deuterated derivatives in that only 60% of the equimolar quantity of oxygen is absorbed.[12] Moreover, the dioxetane is completely absent and is replaced by a new product **15**. This result is readily explained by the following experiment. A slight excess of the norbornene **4** is added to a solution of the dioxetane **5** in neutral methanol at 0 °C. The ether **15** is instantly formed as the only product. This is a new reaction of dioxetanes, which is remarkable for its high regioselectivity.[13] A reasonable mechanism is that the double bond of **4** makes a nucleophilic attack on the C-3 ring oxygen atom of the dioxetane **5** to generate the methoxonium cation **16**.[14,15] Capture of a molecule of methanol gives the ether **15**. When **4** and **5** were mixed in deuteriomethanol then both the *exo*- and *endo*-deuteriomethoxy isomers **17** and **18** were formed in exactly the same ratio as the deuteriomethoxy ketals **10** and **11**, viz., 66:34.

4   5   16   17   18

4   19   20
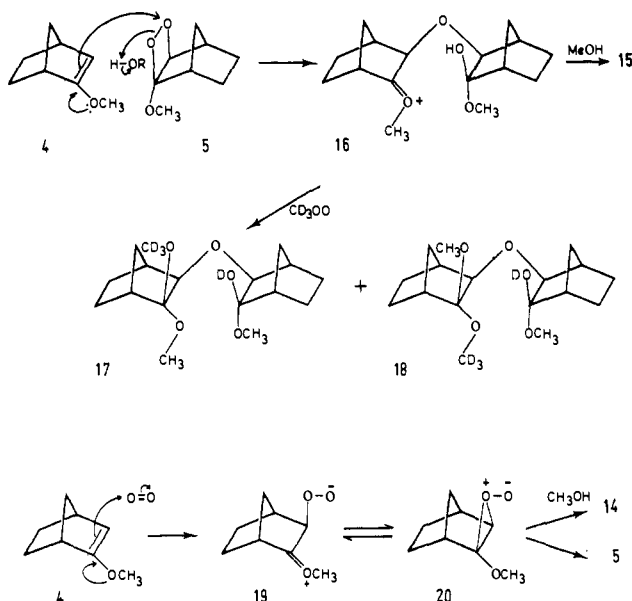
Further tests revealed that the dioxetane **5** is inert toward methanol, deuterated or not, even under the conditions of photooxygenation. All that ultimately occurs is opening to the ester **6** on prolonged irradiation. Further, the hydroperoxides **12** and **13**, as well as **6**, were recovered unchanged after photooxygenation in methanol for 1 h. The norbornene **4** was equally inert to triplet oxygen either on simple irradiation or in the dark.[16]

Consequently, it is safe to assume that **14** arises from a zwitterionic perepoxide which can be formulated as **19** or **20**. In methanol these tautomers would be intercepted to give the hydroperoxide **14**. However, once they rearrange to dioxetane **5**, they remain closed and inert to further reaction with methanol.

These findings parallel those obtained from the photooxygenation in methanol of 2-trimethylsilyloxynorbornene[17] and 1,3-dimethylindole,[18] where zwitterionic peroxides have been invoked. Moreover, they provide chemical evidence for the prediction[19] that such intermediates are separated by a finite

energy barrier from the dioxetane, thereby permitting the chemistry of each species to be discerned.

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(3) The yields of 2-methoxynorborn-2-ene (J. San Filippo, Jr., and G. M. Anderson, *J. Org. Chem.*, **39**, 473 (1974); J. S. MacConaghy, Jr., and J. J. Bloomfield, *ibid.*, **33**, 3425 (1968)) were improved by collecting it over potassium carbonate.
(4) The dioxetane **5** was assayed by iodiometric titration (H. B. Knight and D. Swern, "Organic Syntheses", Collect. Vol. IV, N. Rabjohn, Ed, Wiley, New York, N.Y., 1963, p 895.
(5) Both compounds could be easily purified by column chromatography; however, for safety reasons, as the dioxetane **5** is explosive, experiments with it were carried out in solution.
(6) The photooxygenation was carried out in Pyrex glassware using two cooled 500-W Sylvania FFX projector bulbs screened by Schott-Jena KV 418 filters (cf. C. W. Jefford and A. F. Boschung, *Helv. Chim. Acta*, **57**, 2242 (1974)). Concentrations of **4** were ~0.4 M and of methylene blue ~10^{-3} M. There was no bleaching of the dye. Reaction was rapid; in acetonitrile 100% of absorption of oxygen was reached after some 25 min. The usual tests, e.g., quenching with Dabco, indicated that singlet oxygen was the reagent responsible for oxidation.
(7) K. R. Kopecky, J. E. Filby, C. Mumford, P. A. Lockwood, and J. Y. Ding, *Can. J. Chem.*, **53**, 1103 (1975).
(8) A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Lett.*, 233 (1964).
(9) P. D. Bartlett, A. L. Baumstark, M. E. Landis, and C. L. Lerman, *J. Am. Chem. Soc.*, **96**, 5267 (1974).
(10) All the ketal structures **9**, **10**, and **11**, were established by NMR analysis using shift reagent.
(11) The absence of the *endo*-OCD₃ isomer **11** is puzzling. This *could* be ascribed to a difference in behavior among **7**, **8**, and **16**. On the basis of the precedent set by 2-phenyl-*exo*-2,3-epoxynorbornane (T. J. Gerteisen, D. C. Kleinfelter, G. C. Brophy, and S. Sternhell, *Tetrahedron*, **27**, 3013 (1971)), it might be expected that the 2-methoxy epoxide **8** and perepoxide **20** would similarly undergo exclusive exo attack by methanol. On the other hand, open cations, such as **16** and the phosphorane **7**, incorporate methanol on both the exo and endo sides of the molecule. A further corollary would be that the polar peroxide **19**, unlike its perepoxide tautomer **20**, might be expected to give both exo and endo products.
(12) The lifetime of singlet oxygen in a deuterated solvent is longer than in the parent solvent (P. B. Merkel, R. Nilsson, and D. R. Kearns, *J. Am. Chem. Soc.*, **94**, 1030 (1972)). We have checked that the photooxygenation is a zero-order reaction and thus the rate is a function of the solubility and lifetime of singlet oxygen.
(13) The chemistry of 1,2-dioxetanes has been recently reviewed: W. Adam, *Adv. Heterocycl. Chem.*, **21**, 437 (1977); see also P. D. Bartlett and J. S. McKennis, *J. Am. Chem. Soc.*, **99**, 5334 (1977).
(14) The regioselectivity can be understood firstly by the proverbial exo selectivity of norbornene on reaction with electrophiles. Secondly, the C-3 ring oxygen atom of **5** is expected to be the more electrophilic of the two.
(15) The ionic nature of the proposed push–pull mechanism seems to be confirmed as the reaction still occurs when 2,6-*tert*-butyl-*p*-cresol, a radical inhibitor, is present.
(16) 2-Phenylnorbornene undergoes autooxidation (C. W. Jefford, A. F. Boschung, and C. G. Rimbault, *Helv. Chim. Acta*, **58**, 2542 (1976)).
(17) C. W. Jefford and C. G. Rimbault, *Tetrahedron Lett.*, 2375 (1977).
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Absolute Rates of Hydrogen Abstraction by *tert*-Butoxy Radicals

Sir:

The reactions of *tert*-butoxy radicals have been the subject of numerous studies;[1-5] quite frequently these have been related to the halogenation of organic substrates by *tert*-butyl hypochlorite.[1-3,5c] Despite these studies, the absolute values
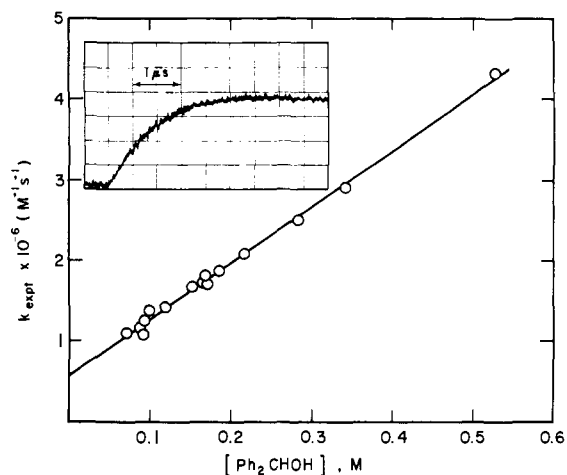
Figure 1. Plot of the experimental pseudo-first-order rate constant vs. the concentration of diphenylmethanol (enclosure: oscilloscope trace for $[Ph_2CHOH] = 0.092$ M as monitored at 535 nm). Each point was obtained by signal average of four-six oscilloscope traces.[9]

Figure 2. Experimental pseudo-first-order rate constants for the buildup of the diphenylhydroxymethyl radical as a function of cumene concentration for two concentrations of diphenylmethanol: ▲, 0.170 M; ●, 0.099 M.

of the rates of reaction of *tert*-butoxy radicals remain unknown. Two studies have attempted the measurement of absolute rate constants.[6] Carlsson and Ingold[2d,e] have examined the photochlorination of toluene by Bu^tOCl using the rotating sector technique. Apart from a number of experimental problems which have been pointed out by the authors, the system employed (toluene–Bu^tOCl) has been the subject of considerable controversy with regard to the actual mechanism, as well as the possible role of chlorine chains.[1f,3b] It seems reasonable to attempt the measurement of absolute rates in an independent system and preferably using time resolved techniques. The other study mentioned above is that of Weiner and Hammond[7] and involved the direct detection of the *tert*-butoxy radicals using ESR spectroscopy. This study has been seriously questioned by Symons[8] who pointed out that the species observed was $Bu^tOOO\cdot$ rather than $Bu^tO\cdot$.

We have examined the reaction of *tert*-butoxy radicals with diphenylmethanol and with cumene using nanosecond laser flash photolysis techniques.[9] The *tert*-butoxy radicals were generated by photodecomposition of di-*tert*-butyl peroxide using the attenuated pulses from a frequency doubled, Q-switched ruby laser (347.1 nm) for excitation.[10]

In the case of diphenylmethanol the resulting ketyl radical (the same as in the photoreduction of benzophenone[11]), has an absorption maximum at ~535 nm.[12] The time profile associated with the buildup of the concentration of ketyl radicals contains information on both the rate of reaction 1 and the lifetime of the *tert*-butoxy radicals as determined by all the other pseudo-first-order modes of decay, reaction 2.
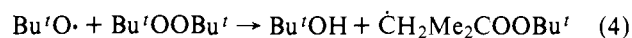
$$Bu^tO\cdot + Ph_2CHOH \rightarrow Bu^tOH + Ph_2\dot{C}OH \quad (1)$$

$$Bu^tO\cdot \rightarrow \text{(first-order decay)} \quad (2)$$
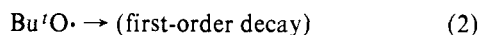
$$k_{expt} = k_2 + k_1[Ph_2CHOH] \quad (3)$$

This treatment assumes that the fate of the *tert*-butoxy radicals is controlled only by first- (or pseudo-first-) order processes. This assumption is correct, provided that the initial radical concentration is kept low enough.[13] The values of k_{expt} were determined from plots of $\ln(A_\infty/A_\infty - A)$ vs. time, where A stands for the absorbance due to $Ph_2\dot{C}OH$ and A_∞ is the plateau value. Figure 1 shows a typical trace for the buildup of $Ph_2\dot{C}OH$ (as monitored at 535 nm) and a plot of k_{expt} vs. $[Ph_2CHOH]$; from this figure we obtain $k_1 = 6.9 \times 10^6$ M^{-1} s^{-1} and $k_2 = 5.7 \times 10^5$ s^{-1} ($k_2 = \tau_{Bu^tO}{}^{-1}$) at room temperature (~22 °C) in 1:2 benzene–di-*tert*-butyl peroxide. From k_2 and the concentration of peroxide we obtain an upper limit
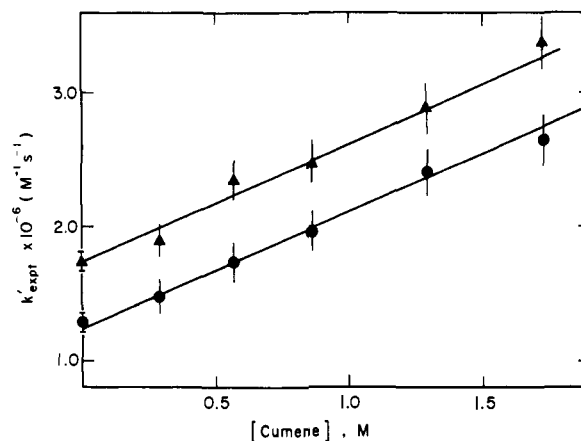
for the rate of reaction 4 as $k_4 \leq 1.6 \times 10^5$ M^{-1} s^{-1} (i.e., 8.8×10^3 M^{-1} s^{-1} on a per-hydrogen basis).

$$Bu^tO\cdot + Bu^tOOBu^t \rightarrow Bu^tOH + \dot{C}H_2Me_2COOBu^t \quad (4)$$

In fact reaction 4 can be expected to represent the main contribution to k_2.[14]

The example given above represents in a way an exception: i.e., most substrates of interest do not produce a free radical which can be easily detected optically under conditions of high pulse attenuation. In these cases the reaction can be monitored in a similar way following the concentration of the diphenylhydroxymethyl radical in a system containing both, diphenylmethanol and as second substrate, RH.

$$Bu^tO\cdot + RH \rightarrow Bu^tOH + R\cdot \quad (5)$$
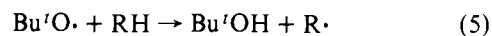
Kinetic analysis of the mechanism shows that the new experimental pseudo-first-order rate constant is now given by

$$k_{expt}' = (k_2 + k_1[Ph_2CHOH]) + k_5[RH] \quad (6)$$

Figure 2 shows two plots of k_{expt}' vs. [RH] for cumene for two different concentrations of diphenylmethanol. The two lines, which were obtained by simultaneous least-squares treatment of both sets lead to k_5[cumene] $= 8.7 \times 10^5$ M^{-1} s^{-1}, while the intercepts, which effectively measure the lifetimes of the *tert*-butoxy radicals in the system, are consistent with the data presented in Figure 1. The carbon-centered radicals produced in reactions 4 and 5 could be expected to decay at least partially via abstraction from diphenylmethanol; however, these processes are around three orders of magnitude slower than the reactions of *tert*-butoxy radicals and can be neglected in the time scale of our experiments.[15]

The rate for cumene is higher than could be expected from previous estimates. For example, for toluene, which is about three times less reactive than cumene,[1e,4] the values measured or estimated before range from 3×10^3 to 9×10^4 M^{-1} s^{-1},[1d,2a,d,4,15] where the highest value is the only one which is not based on the Bu^tOCl reaction.[16]

The absolute rates measured for both substrates compare well with the values for the benzophenone triplet of 5.5×10^5 M^{-1} s^{-1} for cumene and 8.9×10^6 M^{-1} s^{-1} for diphenylmethanol.[11] This similarity was originally pointed out by Walling and Gibian[17] and by Padwa[18] and is widely recognized.[11]

We are currently engaged in the measurement of rate constants, in particular for less reactive and simpler molecules which could serve as reactivity standards for ESR studies of *tert*-butoxy radicals.

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(11) For a review on photoreduction, see J. C. Scaiano, *J. Photochem.*, **2**, 81 (1973/74).

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(19) The research described herein was supported by the Division of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-1801 from the Notre Dame Radiation Laboratory.

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Metal–Carbene Complexes and the Possible Role of Hydroxycarbene in Formaldehyde Laser Photochemistry

Sir:

Hydroxycarbene CHOH is probably the most important very simple carbene which has not been characterized experimentally. First, one would like to relate the properties of hydroxycarbene to those of other simple carbenes (e.g., CH_2, CHF, CHCl, CHBr, and CHCN) for which experimental data is available.[1-3] Secondly, CHOH may be considered the simplest alkoxy carbene A, and alkoxycarbenes have proven ex-
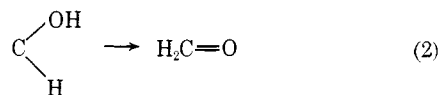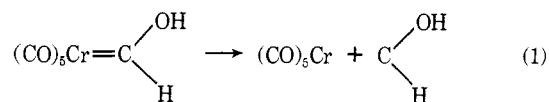
A
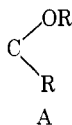
tremely difficult to prepare via conventional synthetic methods.[4,5] Third, the Fischer-type transition metal–carbenes[6] B,

B
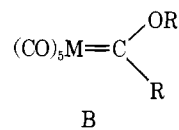
which have been one of the most exciting developments in organometallic chemistry during the past decade, contain the alkoxycarbene fragment. In fact, as related by Fischer in his Nobel address,[7] the very first carbene complexes prepared were of the hydroxy variety C. In fact, metal–carbene complexes

C
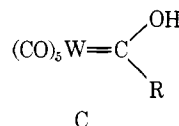
are even today considered[2,7] the most realistic source of the extremely reactive alkoxycarbene radicals. When the carbene ligand is split off from the metal, it appears[7] that a hydrogen shift occurs almost immediately yielding an aldehyde product. A simple example of this process would be

$$(CO)_5Cr{=}C\overset{OH}{\underset{H}{\diagdown}} \longrightarrow (CO)_5Cr + C\overset{OH}{\underset{H}{\diagdown}} \qquad (1)$$

$$C\overset{OH}{\underset{H}{\diagdown}} \longrightarrow H_2C{=}O \qquad (2)$$

Our interest in hydroxycarbene arose from recent experimental studies[8,9] of the laser photodissociation of formaldehyde. Despite the simplicity of this system and the sophistication of the experimental techniques employed, there is still no adequate molecular explanation of the experimental results. Specifically, neither triplet formaldehyde T_1 nor the excited vibrational manifold of the ground state S_0 can be satisfactorily invoked as the intermediate I for the observed process

$$H_2CO(S_0) \xrightarrow{h\nu} H_2CO(S_1) \rightarrow I \rightarrow H_2 + CO \qquad (3)$$
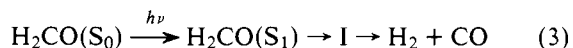
However, if some hitherto unrecognized molecular species were involved in the photodissociation, a coherent picture might emerge. One conceivable such "intermediate state" would be hydroxycarbene,[8] which is of course an isomer of formaldehyde. Here we wish to point out that experiments on Fischer-type carbenes lend credence to this hypothesis. As shown in reaction 1, it is accepted by organometallic chemists[6,7] that hydroxycarbenes spontaneously undergo isomerization to yield formaldehyde. It must be noted of course that the hydroxycarbene in reaction 1 may possess as internal energy some of the exothermicity resulting from the rupture of the metal–carbene bond. Nevertheless, it seems likely that there is a relatively small activation energy for rearrangement 2. This conclusion is indirectly supported by detailed theoretical studies,[10] incorporating the effects of electron correlation, of the related vinylidene rearrangement

$$CH_2{=}C: \rightarrow HC{\equiv}CH \qquad (4)$$

for which a barrier of no more than 8 kcal/mol is predicted.

If there is only a small barrier associated with rearrangement 2, then, from microscopic reversibility, we know that formaldehyde may be converted to hydroxycarbene with an amount of energy only slightly greater than the energy difference between the two isomers. The second purpose of this paper then is to evaluate this energy difference using reliable theoretical techniques. This problem has been addressed in a different