A Kinetic Study of the Reactions of *tert*-Butoxyl with Alkenes: Hydrogen Abstraction vs. Addition[1]

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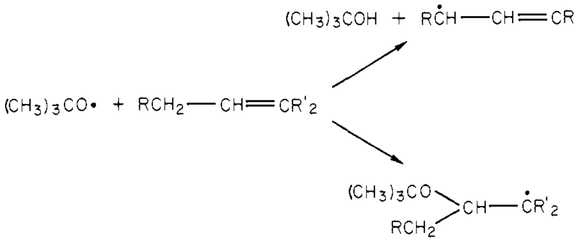
Abstract: Rate constants and Arrhenius parameters have been measured for the reactions of *tert*-butoxyl radicals with alkenes by using laser flash photolysis in benzene–di-*tert*-butyl peroxide (1:2 v/v) as solvent. With norbornene and norbornadiene, additions to the double bonds were the only modes of reaction, whereas with cyclopentene and cyclopentadiene, hydrogen abstraction was a competitive process. The measured activation energies were quite low; thus for norbornene, norbornadiene, and cyclopentene, E_a (kcal/mol) = 2.36 ± 0.40, 1.56 ± 0.55, and 2.35 ± 0.22, respectively, while the corresponding A factors were $\log (A/(M^{-1}\ s^{-1})) = 7.76 \pm 0.31$, 7.65 ± 0.43, and 8.56 ± 0.18. For comparison, hydrogen abstraction by *tert*-butoxyl at cyclopentane proceeds with E_a (kcal/mol) = 3.47 ± 0.59 and $\log (A/(M^{-1}\ s^{-1})) = 8.47 \pm 0.45$.

The reactions of the *tert*-butoxyl radical with hydrocarbon substrates in solution have been the subject of extensive investigation.[2–32] With alkanes the reaction is a simple hydrogen abstraction process[7,8] (reaction 1). However, in the reaction of

$$(CH_3)_3CO\cdot + RH \rightarrow (CH_3)_3COH + R\cdot \qquad (1)$$

alkoxyl radicals with alkenes, two modes of reaction are observed,[4,15,17,24,25,30,32–38] these being hydrogen abstraction at the allylic position and addition to the double bond; see, for example, reactions 2 and 3. In general, the unimolecular fragmentation



(2)

(3)

of *tert*-butoxyl (reaction 4)[3,5,13,20,21,39–43] competes with reactions

$$(CH_3)_3CO\cdot \rightarrow (CH_3)_2CO + \cdot CH_3 \qquad (4)$$

1–3 and has often been used as a kinetic standard or "free-radical clock"[44] allowing the *relative* rate constants for these reactions to be quantified.

While there exists a substantial body of literature on the relative rate constants for the reactions of *tert*-butoxyl with hydrocarbons,[2,5,7–12,15,16,18–25,29,35,40,42] there have been few measurements of absolute rate constants and Arrhenius parameters.[26–28,30,31] To our knowledge, none have been reported for reaction 3, the addition of *tert*-butoxyl to olefins. Even in the case of hydrogen abstraction where the total number of absolute rate constants is somewhat more extensive,[26–28,30,31,36,45–51] Arrhenius parameters have been

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Table I. Kinetic Parameters for the Reaction of *tert*-Butoxyl with Hydrocarbons[a]

hydrocarbon	temp range, K	E_a, kcal/mol[b]	log $(A/(M^{-1}\ s^{-1}))$[b]	k_7,[c] $M^{-1}\ s^{-1}$	reaction type
cyclopentane	236–344	3.47 ± 0.59	8.47 ± 0.45	8.57×10^5	abstraction
cyclopentene	226–304	2.35 ± 0.22[d]	8.56 ± 0.18[d]	6.88×10^6	abstraction + addition
cyclopentadiene	226–330	1.85 ± 0.43[d]	8.21 ± 0.34[d]	7.21×10^6	abstraction + addition
norbornane	246–327	2.91 ± 0.35	7.89 ± 0.27	5.81×10^5	abstraction
norbornene	224–339	2.36 ± 0.40	7.76 ± 0.31	1.09×10^6	addition
norbornadiene	224–347	1.56 ± 0.55	7.65 ± 0.43	3.22×10^6	addition

[a] The solvent was benzene–di-*tert*-butyl peroxide (1:2 v/v) or toluene–di-*tert*-butyl peroxide (1:2 v/v). [b] Errors correspond to 95% confidence limits. [c] Calculated at 300 K. [d] These values represent the measured temperature dependence of k_7 for abstraction plus addition. They are not true activation parameters and are simply a convenient way of reporting the data.

reported for less than ten substrates,[28,48,49,51] only one of them being a simple hydrocarbon (cyclopentane).[28] In this work we attempt to redress this situation and report a detailed kinetic study of these important reactions.

Results and Discussion

Laser flash photolysis was used to determine the overall reactivity of a series of hydrocarbon substrates toward *tert*-butoxyl radicals. Since the transient species of interest in these experiments do not absorb strongly in the visible or near-UV spectrum, diphenylmethanol was used as a probe. This technique has been described in detail elsewhere.[27] Equations 5–8 show the essential part of the kinetic scheme.

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3CO\cdot \tag{5}$$

$$(CH_3)_3CO\cdot + Ph_2CHOH \rightarrow (CH_3)_3COH + Ph_2\dot{C}OH \tag{6}$$

$$(CH_3)_3CO\cdot + \text{hydrocarbon} \rightarrow \text{products} \tag{7}$$

$$(CH_3)_3CO\cdot \rightarrow \text{pseudo-first-order decay} \tag{8}$$

Reaction 6 leads to the generation of the diphenylhydroxymethyl radical, which has a strong optical absorption at 540 nm[30,52] and is therefore easily monitored. Reaction 7 represents the sum of all possible reactions of the hydrocarbon substrate with *tert*-butoxyl. With alkenes this composite includes both hydrogen abstraction and addition (reactions 2 and 3). Clearly, additional experiments are required to quantify the relative contributions due to these two processes (vide infra).

Reaction 8 includes the attack of *tert*-butoxyl on its parent peroxide and its β scission to acetone and the methyl radical. Under the experimental conditions used in this work, the latter reaction is relatively unimportant. In most cases the concentrations of substrate and diphenylmethanol are high enough so as to make reactions 6 and 7 the predominant decay processes.

In addition to reactions 4–8, radical–radical reactions can be significant at high excitation doses. In these experiments the intensity of the laser pulse was attenuated by using neutral density filters to eliminate such contributions.[27] In all cases, a clean first-order growth due to the diphenylhydroxymethyl radical was detected after the laser pulse. The rate constant for this growth (k_{exptl}) is related to the rate constants of interest as follows:

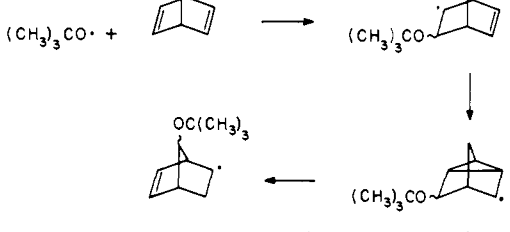
$$k_{\text{exptl}} = k_8 + k_6[Ph_2CHOH] + k_7[\text{hydrocarbon}] \tag{9}$$

A plot of k_{exptl} vs. the concentration of the hydrocarbon substrate at constant diphenylmethanol yields k_7.[27] Thus, in a typical experiment, a series of samples containing a specific concentration of diphenylmethanol (usually about 0.1 M) and variable concentrations of hydrocarbon were prepared. At room or higher temperatures a 1:2 (v/v) mixture of benzene–di-*tert*-butyl peroxide was used as a solvent, while at lower temperatures a 1:2 (v/v) mixture of toluene-d_8–di-*tert*-butyl peroxide was used in preference. Values of k_{exptl} were obtained by monitoring the growth of the signal due to diphenylhydroxymethyl at 540 nm. Values of k_7 obtained in the two solvents at 27 °C were the same within experimental error (±10%). They are summarized in Table I.

As mentioned above, the rate constants reported for k_7 represent the overall reactivity of the hydrocarbon substrate toward *tert*-butoxyl. A number of experiments were therefore carried out to measure the relative importance of addition vs. abstraction in the alkenes used in this work.

A series of measurements of the relative quantum yields of *tert*-butyl alcohol formation were carried out in experiments where di-*tert*-butyl peroxide was photolyzed in the presence of hydrocarbon substrates. Cyclopentane was used as a reference substrate and was therefore effectively an actinometer. In this case, hydrogen abstraction was the major pathway for the decay of *tert*-butoxyl (i.e., *tert*-butyl alcohol/acetone > 10). The percentage of reaction that proceeds via addition of *tert*-butoxyl at room temperature was found to be 10% for cyclopentene, 60% for cyclopentadiene, and 100% for both norbornene and norbornadiene. For cyclopentene and cyclopentadiene, these estimates may be lower limits if reaction 3 is reversible under the reaction conditions.

EPR studies were carried out at various temperatures between −120 and +40 °C in isooctane or cyclopropane solvent. When di-*tert*-butyl peroxide was photolyzed in the presence of cyclopentene, the only observable radical was cyclopentenyl, although the noise level was substantial at temperatures above −20 °C. In the case of cyclopentadiene at −120 °C, both the cyclopentadienyl and the 4-*tert*-butoxycyclopent-1-en-3-yl radical were detected, as reported by Kochi et al.[17] Double integration of suitable lines from each radical led to a 6.5:1.0 ratio for addition to abstraction at −120 °C. The intensity of the broad lines from the adduct radical weakened considerably when the temperature was raised and were hardly detectable above −20 °C. In the case of norbornene, the only signal observed was a weak multiplet with broad overlapping lines, which is probably the adduct radical, since spectra due to the norbornenyl and nortricyclyl radicals were absent.[32] With norbornadiene, the results obtained were the same as reported earlier. That is, addition of *tert*-butoxyl was the only detectable process, and the resulting norbornenyl radical underwent rearrangement at the appropriate temperatures (reaction 10).[32]



(10)

tert-Butoxyls show a pronounced tendency to undergo hydrogen abstraction reactions where allylic hydrogens are available;[36] this tendency is not shown in the case of norbornene and norbornadiene simply because of geometrical or stereoelectronic effects that would

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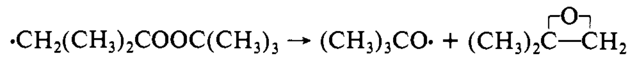
prevent the delocalization of the unpaired electron on the double bond(s). In other words, while the resulting radicals are formally allylic, the resonance stabilization is minimal. In the five-membered rings, hydrogen abstraction is quite important and predominates in the case of cyclopentene. As is frequently the case, the behavior of *tert*-butoxyl parallels that of ketone triplets, particularly benzophenone,[30,53–56] and contrasts that of benzoyloxy radicals, which generally show a preference for addition to unsaturated systems[17,57–60] rather than hydrogen abstraction.

The only substrate for which a direct comparison with absolute kinetic parameters obtained earlier is possible is the case of cyclopentane, which was examined by Wong[28] using flash photolysis EPR techniques (FPESR). The rate constants reported by Wong are around one-half of those reported herein, which, in view of the large differences in experimental approach, can be regarded as satisfactory agreement. However, Wong reports $E_a = 6.1 \pm 0.3$ kcal/mol and $\log (A/(\mathrm{M^{-1}\,s^{-1}})) = 10.1 \pm 0.2$; both values are substantially higher than those given in Table I, and the differences are well beyond the estimated error limits. While the source of the difference cannot be conclusively established at this point, our determination of the Arrhenius parameters is based on a wide temperature range (108° compared with less than 50° in Wong's[28] measurements), and the time scales involved are well within the time resolution of the technique. By contrast, in the case of FPESR (where 100-kHz modulation was used), the accuracy of radical lifetimes of a few tens of microseconds may be questionable. On the other hand, it has been pointed out[28] that reactions 11 and 12 could introduce some error in the laser photolysis measurements.[61]

$$\mathrm{(CH_3)_3CO\cdot + (CH_3)_3COOC(CH_3)_3 \rightarrow (CH_3)_3COH + \cdot CH_2(CH_3)_2COOC(CH_3)_3} \qquad (11)$$



$$\mathrm{\cdot CH_2(CH_3)_2COOC(CH_3)_3 \rightarrow (CH_3)_3CO\cdot + (CH_3)_2\overbrace{C{-}CH_2}^{O}} \qquad (12)$$

Reaction 12 is unlikely to play an important role in our systems because reaction 11 is usually only a minor mode of *tert*-butoxyl decay.[26,27,30,31,36,45–51,62] However, in connection with the current study, we decided to examine this question in some detail. The following experiment can be regarded as a good diagnostic test: If *tert*-butoxyl radicals are generated *thermally* from di-*tert*-butoxyl peroxyoxalate in the presence of di-*tert*-butyl peroxide (which is stable at the temperature of this experiment, 40 °C) and a substrate such as cyclopentane, one should expect a significant decrease in peroxide concentration if reaction 11 occurs to a substantial degree. When such an experiment was carried out (see Experimental Section), the outcome was a slight (~3%) *increase* in peroxide concentration. While this experiment does not throw light on the kinetics of processes 11 and 12, it does show conclusively that the role of reaction 12 can be safely ignored under our experimental conditions.

Experimental Section

Materials. All of the hydrocarbons used in this work were commercially available except for cyclopentadiene, which was prepared by standard procedures.[63] They were distilled before use, and in all cases their purity was >99% (VPC analysis). Di-*tert*-butyl peroxide (K&K or MC&B) was purified by column chromatography on alumina. Benzene (Aldrich, Gold Label) was treated with concentrated sulfuric acid and was washed and neutralized before being distilled from calcium hydride under a nitrogen atmosphere. Diphenylmethanol (Eastman Kodak) was freshly sublimed. Toluene-d_8 (Merck, Sharp and Dohme) was used as received. Di-*tert*-butyl peroxyoxalate was prepared by established procedures.[64]

All of the samples used in this work were carefully deoxygenated by nitrogen purging or by using freeze–pump–thaw degassing cycles.

Apparatus. EPR experiments were carried out with a Varian E104 spectrometer equipped with a 500-W high-pressure mercury lamp. The output from the lamp was filtered through a cobalt–nickel solution to remove much of the visible and most of the infrared radiation.

The laser flash photolysis equipment has been described in detail elsewhere.[65] Briefly, the pulses (337.1 nm, ~8 ns, up to 10 mJ) from a Molectron UV-24 nitrogen laser were used for excitation. Transient absorbances were monitored by using a detection system with nanosecond response. Signals from the detector system were processed through an R-7912 Tektronix transient digitizer and were analyzed by using a dedicated PDP11-03L computer, which also provided storage and hardcopy facilities.

Photochemical Experiments. A series of experiments were carried out to determine the relative quantum yields of *tert*-butyl alcohol when di-*tert*-butyl peroxide (3 M) was photolyzed in the presence of hydrocarbon substrates (~1 M) in Freon 113 solvent. The solutions were deoxygenated by freeze–pump–thaw degassing cycles and were photolyzed in a Rayonet reactor equipped with an RPR-3000 lamp. The samples were photolyzed until ca. 1% of the initial di-*tert*-butyl peroxide had been destroyed and were then analyzed by VPC (on 20% Carbowax 20 M).

Thermal Decomposition of Di-*tert*-butyl Peroxyoxalate in the Presence of Di-*tert*-butyl Peroxide. Di-*tert*-butyl peroxyoxalate (0.115 g, 0.5 mmol) was heated at 40 °C for 2 h with a mixture of di-*tert*-butyl peroxide (0.365 g, 1.25 mmol), cyclopentane (0.175 g, 1.25 mmol), and benzene (also used as internal standard, 0.195 g, 1.25 mmol). After this time, all the peroxyoxalate had been consumed. VPC analysis showed that 28% of the cyclopentane had been consumed, while the concentration of di-*tert*-butyl peroxide had increased by 3%. Quite possibly, this increase results from cage recombination of *tert*-butoxyl radicals, as suggested by the formation of peroxide in a control experiment in which the peroxyoxalate was decomposed in a mixture of cyclopentane, benzene, and Freon 113.

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Registry No. Cyclopentane, 287-92-3; cyclopentene, 142-29-0; cyclopentadiene, 542-92-7; norborane, 279-23-2; norbornene, 498-66-8; norbornadiene, 121-46-0; *tert*-butoxyl, 3141-58-0; hydrogen, 1333-74-0.

Supplementary Material Available: Six tables (II–VII) giving detailed kinetic data (16 pages). Ordering information is given on any current masthead page.

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