Electron Spin Resonance Study of Addition of Alkoxy Radicals to Olefins

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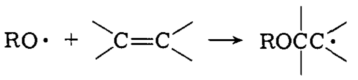
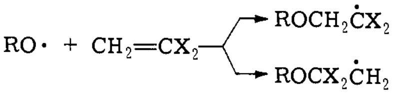
Abstract: The additions of alkoxy radicals generated during photolysis of various peroxides in the presence of ethylene, isobutylene, vinylidene fluoride, or 1,3-butadiene are examined in solution by esr techniques. The *tert*-butoxy radical shows unusual and unique behavior among various oxygen-centered species, including methoxy, *n*- and isopropoxy, *n*- and *sec*-butoxy, trifluoromethoxy, trimethylsiloxy, alkoxycarboxy, and benzoyloxy radicals in (i) its slow addition to ethylene, (ii) its high rate of allylic hydrogen abstraction from isobutylene relative to addition, and (iii) its regiospecific addition to the difluoromethylene terminus of vinylidene fluoride. However, the difference among alkoxy radicals is minimal in their addition to the more reactive 1,3-butadiene, and adducts are observed with all alkoxy radicals. Photolysis of primary and secondary alkyl peroxides afford alkoxy adducts with isobutylene and 1,3-butadiene, but only the spectra of acyl and α-hydroxyalkyl radicals, respectively, from the induced decomposition of the peroxides are observed in the presence of the less reactive ethylene.

Addition of free radicals to alkenes and alkynes constitutes an important route to the formation of C–C bonds in synthesis and polymerization or telomerization processes.[1] In particular, the formation of carbon–oxygen bonds results from the addition of oxygen-centered radicals RO· to carbon–carbon multiple bonds, *e.g.*



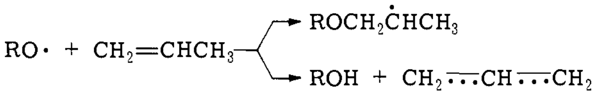
The formation of these radical adducts is tantamount to substitution of oxygen in the β position of alkyl radicals. The presence of heteroatoms in the β positions of alkyl radicals may have important stereochemical consequences as studies of bridged free radicals have shown.[2]

Additions to unsymmetrical olefins raise additional questions regarding the orientations in free radical additions.



$$RO\cdot + CH_2{=}CX_2 \rightarrow ROCH_2\dot{C}X_2 \quad ; \quad RO\cdot + CH_2{=}CX_2 \rightarrow ROCX_2\dot{C}H_2$$

Furthermore, if allylic hydrogens are present in the olefin, competition exists between addition and abstraction, *e.g.*[3]



$$RO\cdot + CH_2{=}CHCH_3 \rightarrow ROCH_2\dot{C}HCH_3 \quad ; \quad RO\cdot + CH_2{=}CHCH_3 \rightarrow ROH + CH_2\cdots CH\cdots CH_2$$

Previous studies have shown how electron spin resonance (esr) techniques can be used to identify various transient free radicals in solution and to deduce their structures and conformations.[4] The study of oxygen-centered radicals merits particular attention since there are indications that their reactivity is highly dependent on their structure.[5] For example, *tert*-butoxy radicals appear to be uniquely disposed toward allylic hydrogen abstraction, and they afford well-resolved esr spectra of the corresponding allyl radical with little or no interference from the adduct when they react with propylene or isobutylene in solution.[6,7] On the other hand, other oxygen-centered radicals yield predominantly the spectra of adducts under the same conditions.[5,8,9]

We have employed esr techniques in this study to identify the principal alkyl radical species formed during the exposure of various alkoxy radicals to olefins. Ethylene, isobutylene, vinylidene fluoride, and 1,3-butadiene were chosen to cover a typical spectrum of olefinic structures. Since the method used in this study relies on the continuous photolysis of peroxides, kinetic processes must be related to the observation of radicals under (quasi) steady-state conditions.

Results

Addition of Alkoxy Radicals to Ethylene. An intense and well-resolved esr spectrum of β-trifluoromethoxyethyl radical (Ia) is readily observed during ultraviolet irradiation of a solution of bis(trifluoromethyl) peroxide and ethylene in cyclopropane solution.[8]

$$CF_3OOCF_3 + CH_2{=}CH_2 \xrightarrow{h\nu} \underset{\text{Ia}}{CF_3OCH_2CH_2\cdot} \qquad (1)$$

On the other hand, a similar study using di-*tert*-butyl peroxide affords no spectrum corresponding to that of an adduct Ib to ethylene. Instead only a weak spectrum of cyclopropyl radical resulting from hydrogen abstraction from the solvent is observed.

$$(CH_3)_3COOC(CH_3)_3 + CH_2{=}CH_2 \xrightarrow{h\nu} \underset{\text{Ib}}{(CH_3)_3COCH_2CH_2\cdot} \qquad (2)$$

We also examined the photolysis of di-*tert*-butyl peroxide and ethylene in the presence of boron trifluoride since there are reports that additions of amino radicals to alkenes are facilitated by complexing the lone electron pair on nitrogen.[12] However, we were still unable to observe the esr spectrum of the *tert*-butoxy adduct even under these modified conditions.

When the mixed peroxide, *tert*-butyl methyl peroxide, is similarly photolyzed in ethylene solution, the esr spectrum of only β-methoxyethyl radical Ic shown in Figure 1a is observed.

$$(CH_3)_3COOCH_3 + CH_2{=}CH_2 \xrightarrow{h\nu} \underset{\text{Ic}}{CH_3OCH_2\dot{C}H_2} \qquad (3)$$

The assignment is based on the same esr parameters ($\langle g\rangle = 2.00258$, $a_{\alpha H} = 22.21$ G, $a_{\beta H} = 32.00$ G at $-75°$) with those of β-methoxyethyl radical generated independently and unambiguously from bis-β-methoxypropionyl peroxide (Figure 1b).[8]

$$CH_3OCH_2CH_2CO_2O_2CCH_2CH_2OCH_3 \xrightarrow{h\nu} 2CH_3OCH_2CH_2\cdot + 2CO_2 \qquad (4)$$

There is clearly no indication in Figure 1a for the presence of the adduct Ib expected from the *tert*-butoxy moiety, *viz.*, β-*tert*-butoxyethyl radical.[13] The latter can be generated unambiguously from β-*tert*-butoxyethyl bromide and silyl radicals as shown in Figure 1c by a general procedure that has been tested extensively.[9,14]

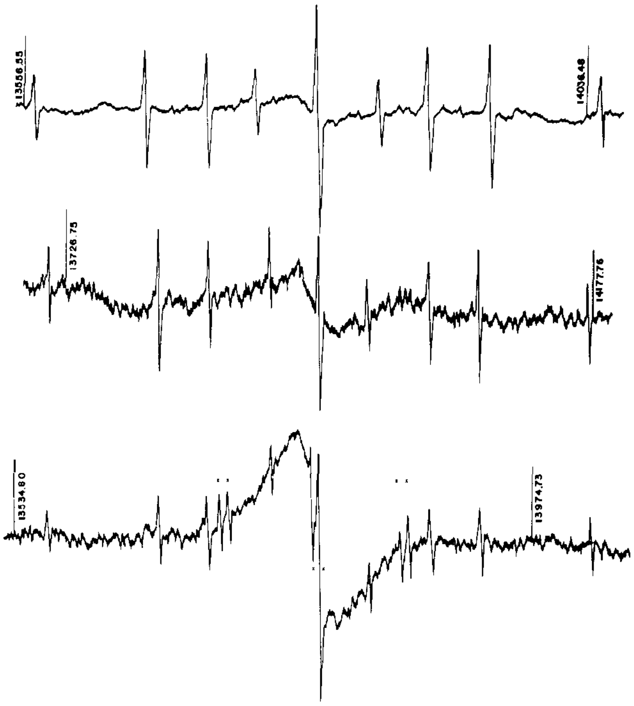


Figure 1. Lower: esr spectrum obtained during photolysis of *tert*-butyl methyl peroxide in isobutylene solutions at −110°. Lines marked with "x" are due to the hydroxymethyl radical. Middle: esr spectrum of methoxyethyl radical from $CH_3OCH_2CH_2Br$ and Et_3Si at −78°. Upper: esr spectrum of *tert*-butoxyethyl radical from $(CH_3)_3COCH_2CH_2Br$ and Et_3Si at −124°.

$$(CH_3)_3COCH_2CH_2Br + Et_3Si\cdot \longrightarrow Et_3SiBr + \underset{\text{Ib}}{(CH_3)_3COCH_2CH_2\cdot} \quad (5)$$

Indeed, a variety of β-alkoxyethyl radicals can be produced from the corresponding β-alkoxyethyl bromides for esr study.[5,9] The esr parameters ($\langle g \rangle = 2.00254$, $a_{\alpha H} = 22.04$ G, and $a_{\beta H} = 35.06$ G at −114°) and the negative temperature dependence of the β-proton hyperfine splitting in the *tert*-butoxyethyl radical are similar to those shown by other β-alkoxyethyl radicals as well as the hydrocarbon analogs, such as *n*-butyl radical.[8,11]

The relatively high signal-to-noise level shown in the esr spectrum of *tert*-butoxyethyl radical is similar to that of other β-alkoxyethyl radicals and characteristic of quality spectra obtainable for analogous primary alkyl radicals generated under similar conditions.[4] Thus, comparable lifetimes or stabilities are indicated for both alkyl and β-alkoxyethyl radicals, and we deduce that the latter, even β-*tert*-butoxyethyl radical, exhibits no unusual tendency for β elimination.[15]

$$(CH_3)_3COCH_2CH_2\cdot \longrightarrow (CH_3)_3CO\cdot + CH_2{=}CH_2 \quad (6)$$

The foregoing studies indicate that our ability to observe only the spectrum of the methoxy adduct Ic to ethylene during photolysis of *tert*-butyl methyl peroxide cannot be due to the instability of the *tert*-butoxy analog. Furthermore, *tert*-butyl methyl peroxide is not unique since another mixed peroxide, *viz*., *tert*-butyl trimethylsilyl peroxide, shows the same behavior, and photolysis of ethylene solutions affords only the esr spectrum of the trimethylsiloxy adduct Id.[9]

$$(CH_3)_3COOSi(CH_3)_3 + CH_2{=}CH_2 \xrightarrow{h\nu} \underset{\text{Id}}{(CH_3)_3SiOCH_2CH_2\cdot} \quad (7)$$

These esr studies measure the (quasi) steady-state concentrations of radicals extant in solution during photolysis. We expect that the relative concentrations of the adducts derived from the photolysis of methyl *tert*-butyl peroxide in ethylene solution mainly reflect their rates of formation since the rates of the bimolecular reactions of methoxyethyl radical should be about the same or even faster than those of *tert*-butoxyethyl radical.[6b] On this basis, we conclude that the addition of *tert*-butoxy radical to ethylene occurs significantly slower than that of other alkoxy radicals, including methoxy.

We sought next the effect of branching at the α carbon in alkoxy radicals as a factor influencing the rate of addition to ethylene. However, primary and secondary alkoxy radicals suffer from the presence of readily abstractable α hydrogens. Thus, di-*n*-butyl peroxide and di-*n*-propyl peroxide when photolyzed in ethylene solution afforded only the esr spectrum *n*-butyryl radical (singlet, $\langle g \rangle = 2.0071$) and propionyl radical (singlet, $\langle g \rangle = 2.0070$), respectively.[16] The formation of acyl radicals as principal intermediates in the photolysis of these primary alkyl peroxides is related to the facile induced decomposition by a pathway involving abstraction of an α hydrogen such as:[16]

$$RCH_2OOCH_2R + RCH_2O\cdot \longrightarrow RCH_2OH + R\dot{C}HOOCH_2R \quad (8a)$$

$$R\dot{C}HOOCH_2R \longrightarrow RCHO + RCH_2O\cdot \quad (8b)$$

$$RCHO + RCH_2O\cdot \longrightarrow RCH_2OH + R\dot{C}O \quad (8c)$$

To minimize decomposition by this route, we carried out the reactions at very low peroxide concentrations, but even under these conditions no spectrum of the adduct was observed. The photolyses were also carried out at temperatures as high as −40° but without success.

Di-*sec*-butyl peroxide and diisopropyl peroxide under the same conditions, after a few minutes photolysis, gave only esr signals derived from radicals produced by hydrogen abstraction of alcohols formed during photolysis.[18] Thus, the

$$R'RCHO\cdot + R'RCHOOCHR'R \longrightarrow R'RCHOH + R'R\dot{C}OOCHR'R \quad (9a)$$

$$R'RCHO\cdot + R'RCHOH \longrightarrow R'R\dot{C}OH + R'RCHOH \quad (9b)$$

spectra of 2-hydroxy-2-butyl radical ($a^{\alpha}{}_{CH_3} = 19.44$ G and $a_{CH_2} = 16.78$ G; $a^{\beta}{}_{CH_3} = a_{OH}$ not resolved; $\langle g \rangle = 2.00310$) and 2-hydroxy-2-propyl radical ($a_{CH_3} = 19.35$ G and $a_{OH} = 0.93$ G: $\langle g \rangle = 2.00316$) were observed from the *sec*-butyl and isopropyl peroxides, respectively. There was no evidence of radicals produced by hydrogen abstraction from the ketonic products.[19]

Other sources of alkoxy radicals were also examined in attempts to obviate problems associated with the induced decomposition of dialkyl peroxides. Photolysis of *tert*-butyl peracetate in ethylene solutions afforded only the esr spectrum of the methyl radical. The spectrum observed under

$$CH_3CO_2\text{-}O\text{-}t\text{-}Bu \xrightarrow[CH_2=CH_2]{h\nu} CH_3\cdot + CO_2 + t\text{-}BuO\cdot \quad (10)$$

the same conditions from *n*-butyl peracetate only consisted of the superposition of the spectrum of methyl radical on that of *n*-butyryl radical, and there was no evidence of an adduct radical. Similarly unsuccessful was the photolysis of *n*-butyl nitrite in ethylene solutions, which gave the esr spectra of only nitrogen-containing radicals readily identified by the 1:1:1 triplets.

$$n\text{-}BuONO \xrightarrow[CH_2=CH_2]{h\nu} n\text{-}BuO\cdot + NO,\ \text{etc.} \quad (11)$$

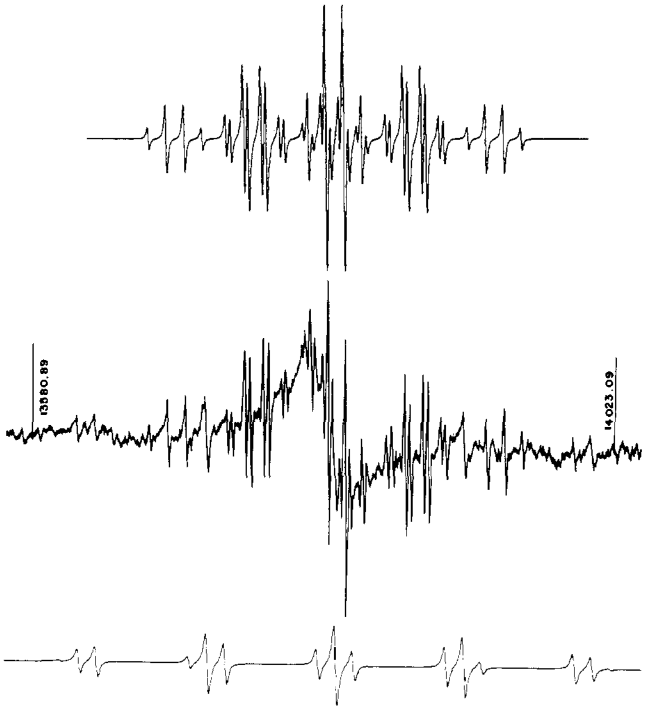


Figure 2. Middle: esr spectrum obtained during photolysis of di-*tert*-butyl peroxide in isobutylene solutions at −40°. Lower: computer-simulated spectrum of $(CH_3)_3COCH_2\dot{C}(CH_3)_2$ from experimental esr parameters in Table I. Upper: simulated spectrum of 2-methallyl radical from experimental parameters in ref 7. Note: relative intensities of simulated spectra to approximate the experimental spectrum.

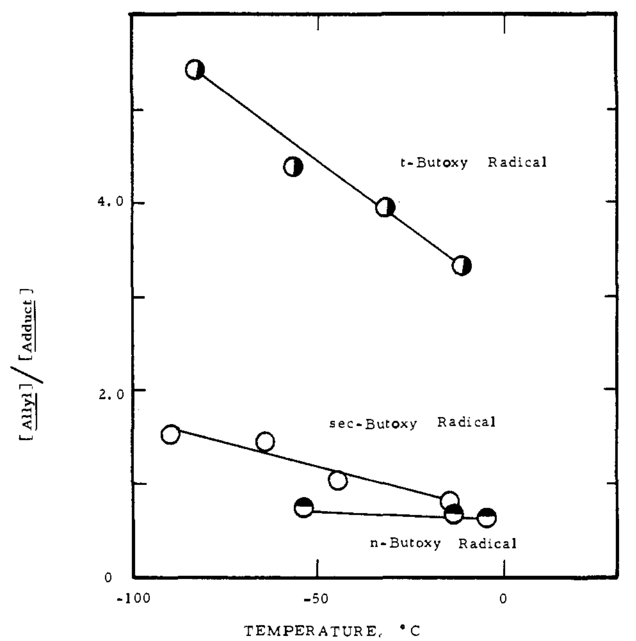


Figure 3. Temperature dependence of the relative steady-state concentrations of 2-methallyl radical and the alkoxy adduct to isobutylene. (◑) *t*-BuO, (○) *sec*-BuO, and (◒) *n*-BuO.

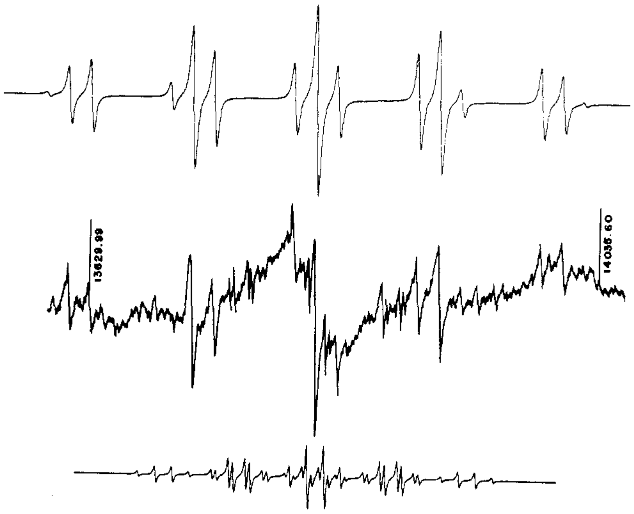


Figure 4. Middle: esr spectrum obtained during photolysis of di-*n*-butyl peroxide in isobutylene solutions at −80°. Upper: computer-simulated spectrum of $n\text{-}BuOCH_2\dot{C}(CH_3)_2$ using the experimental parameters in Table I. Lower: simulated spectrum of 2-methallyl radical from the hfs in ref 7. Note: relative intensities of the simulated spectra to approximate the experimental spectrum.

Addition of Alkoxy Radicals to Isobutylene. Isobutylene represents an unsymmetrically substituted olefin which is not only more electron rich than ethylene but also has an abstractable allylic hydrogen. Addition to isobutylene generates a tertiary alkyl radical adduct II.

$$CH_2{=}C(CH_3)_2 + RO\cdot \begin{cases} \xrightarrow{k_{add}} \underset{\text{II}}{ROCH_2\dot{C}(CH_3)_2} & (12) \\ \xrightarrow{k_{abs}} ROH + CH_2{=}C(CH_3)CH_2\cdot & (13) \end{cases}$$

The photolysis of di-*tert*-butyl peroxide in isobutylene solutions at temperatures lower than *ca.* −90° afforded only the esr spectrum of the 2-methallyl radical III. At higher temperatures, the esr spectrum in Figure 2 consisted of the superposition of two spectra, corresponding to the allylic radical III and the adduct radical II in which R = $(CH_3)_3CO$. The spectrum of the latter was derived unambiguously from reaction 15 of the corresponding β-*tert*-butoxy alkyl bromide and triethylsilyl radical. The computer-

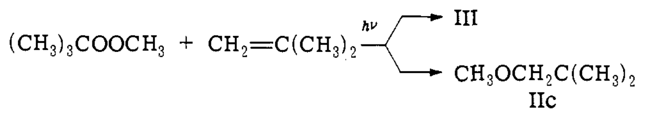
$$(CH_3)_3COOC(CH_3)_3 + CH_2{=}C(CH_3)_2 \begin{cases} \longrightarrow \underset{\text{III}}{CH_2{=}C(CH_3)CH_2\cdot} + (CH_3)_3COH & (14a) \\ \longrightarrow \underset{\text{IIa}}{(CH_3)_3COCH_2\dot{C}(CH_3)_2} & (14b) \end{cases}$$

$$(CH_3)_3COCH_2C(CH_3)_2Br + Et_3Si\cdot \longrightarrow \text{IIa} + Et_3SiBr \quad (15)$$

simulated spectra of IIa and III are also shown in Figure 2 for ready comparison. The steady-state concentration of the adduct IIa increased relative to that of methallyl radical as the temperature was increased as shown in Figure 3.

Photolysis of solutions of isobutylene and other symmetrical dialkyl peroxides also gave rise to esr spectra consisting of two species, II and III, the relative steady-state concentrations of which were temperature-dependent and characteristic of the alkoxy moiety shown in Figure 3. Thus, the principal species observed by esr during photolysis of di-*n*-butyl peroxide in isobutylene solution in Figure 4 is the adduct IIb (II, R = $n\text{-}C_4H_9$), together with only minor amounts of 2-methallyl radical. The esr spectrum of IIb was generated independently from $n\text{-}BuOCH_2C(CH_3)_2Br$ and triethylsilyl radical. The spectra of III and IIb were simulated from the experimental coupling constants and are shown in Figure 4 for comparison with the experimental spectrum.

Photolysis of the mixed peroxide, methyl *tert*-butyl peroxide, in isobutylene solution at −68° afforded a composite spectrum consisting of at least two species. The minor component was readily identified as 2-methallyl radical, and the more important species was clearly derived from the isobutylene adduct II since the hyperfine splitting consisted of a septet ($a_{(CH_3)_2}$ = 23 G) of triplets ($a^{\beta}{}_{CH_2}$ = 18 G). The



$$(CH_3)_3COOCH_3 + CH_2{=}C(CH_3)_2 \xrightarrow{h\nu} \begin{cases} III \\ CH_3OCH_2\dot{C}(CH_3)_2 \end{cases}$$

IIc

latter probably corresponds to IIc since the esr parameters are the same as those of $CH_3OCH_2\dot{C}(CH_3)_2$ generated from 1-methoxy-2-methyl-2-propyl bromide and triethylsilyl radicals. However, the presence of the *tert*-butoxy adduct IIa in small amounts cannot be readily ascertained since the hyperfine splittings of IIa and IIc are comparable.

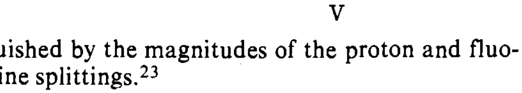
The esr spectra of the alkoxy adducts to isobutylene have similar values for the α-methyl and β-methylene proton splittings as listed in Table I (see paragraph at the end of this paper regarding supplementary material). In all these adducts, the β-methylene splittings are substantially less than those in the ethylene adducts and are more or less temperature independent.

It is interesting to relate the relative steady-state concentrations of 2-methallyl and adduct radicals II and III obtained by esr to the kinetics of hydrogen abstraction and addition in eq 12 and 13. Qualitatively, Figure 3 shows a significantly greater tendency for *tert*-butoxy radicals to undergo abstraction compared with either *sec*-butoxy or *n*-butoxy radicals. Isopropoxy and *n*-propoxy radicals examined at two temperatures also favored addition, but the low signal-to-noise levels in the spectra precluded accurate determinations of the relative concentrations of II and III. The relative amounts of abstraction and addition, given by k_{abs}/k_{add}, in eq 12 and 13, have been measured by Walling and Thaler from product studies to be 7.3 at −78° and 5.8 at 40° for the reaction between *tert*-butoxy radicals and isobutylene.[20] If we assume that II and III are only formed by eq 12 and 13, respectively, and disappear by the three bimolecular routes with rate constants k_m, k_a, and k_c (representing the self and cross reactions of methallyl and adduct radicals), then the steady-state expression is:

$$\frac{k_{abs}}{k_{add}} = \frac{[III]}{[II]}\left\{\frac{k_m[III] + k_c[II]}{k_a[II] + k_c[III]}\right\} \qquad (16)$$

Extrapolation of the data in Figure 3 indicates that [III]/[II] = 2.3 at 25°. The bimolecular rate constants for self-reactions of 2-methyllyl radical and *tert*-butyl radical have been evaluated as 6.7×10^9 and 2.2×10^9 l. mol^{-1} sec^{-1} at 25°, respectively.[21] If we approximate k_a to be the same as that for *tert*-butyl radical and k_c to be the geometric mean of k_m and k_a, we calculate k_{abs}/k_{add} to be 4 at 25°. Considering the assumptions made, this ratio of rate constants determined by esr represents a reasonable comparison with a value of 5 interpolated from Walling and Thaler's data.

Addition of Radicals to Vinylidene and Vinyl Fluorides. I. Vinylidene fluoride represents an unsaturated compound that is sterically somewhat analogous to isobutylene but has opposed charge requirements due to the electronegative geminal fluorines.[22] Addition may occur at either carbon center as indicated in eq 17. The isomeric adducts IV and V



$$X\cdot + CH_2{=}CF_2 \rightarrow \begin{cases} XCH_2\dot{C}F_2 & (17a) \\ \text{IV} & \\ XCF_2\dot{C}H_2 & (17b) \\ \text{V} & \end{cases}$$

are distinguished by the magnitudes of the proton and fluorine hyperfine splittings.[23]

Photolysis of bis(trifluoromethyl) peroxide in solutions containing vinylidene fluoride affords a well-resolved and

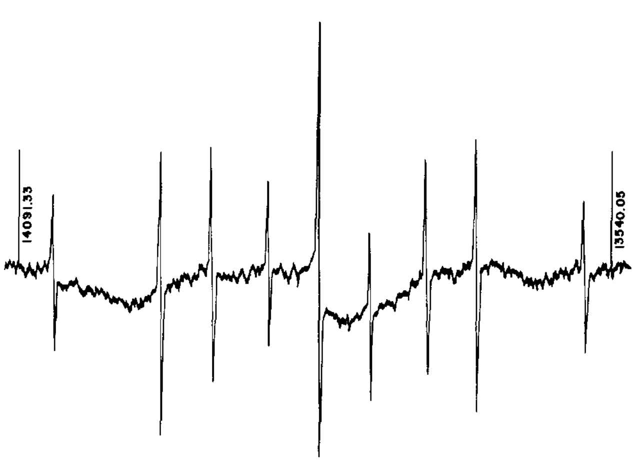


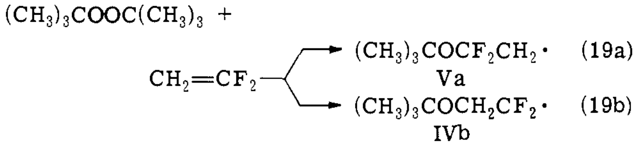
Figure 5. Esr spectrum of $(CH_3)_3COCF_2CH_2$ obtained from the reaction of triethylsilyl radicals and the adduct of *tert*-butyl hypochlorite to vinylidene fluoride in cyclopropane solution at −120°. Proton nmr field markers are in kilohertz.

intense esr spectrum of only IVa (IV, X = CF_3O). The ad-

$$CF_3OOCF_3 + CH_2{=}CF_2 \xrightarrow{h\nu} \underset{\text{IVa}}{CF_3OCH_2CF_2} \qquad (18)$$

dition of trifluoromethoxy radical to the methylene terminus of vinylidene fluoride to form adducts IV coincides with the addition of the sulfur-centered alkylthiyl radicals, silicon-centered trialkylsilyl radicals, and chlorine atoms with the same regiospecificity.[23] These orientations, based on the observation of the esr spectra of the adducts, are generally supported by product studies. In the interpretation of product studies, however, care must be exercised with some radicals to take into account the possibility of reversibility in the addition step.

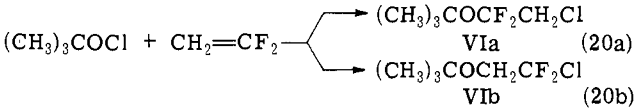
Surprisingly the photolysis of di-*tert*-butyl peroxide in the presence of vinylidene fluoride afforded only the esr spectrum of adduct Va, corresponding to the addition of



$$(CH_3)_3COOC(CH_3)_3 + CH_2{=}CF_2 \rightarrow \begin{cases} (CH_3)_3COCF_2CH_2\cdot & (19a) \\ \text{Va} & \\ (CH_3)_3COCH_2CF_2\cdot & (19b) \\ \text{IVb} & \end{cases}$$

tert-butoxy radical to the difluoromethylene terminus. The esr parameters of Va [⟨g⟩ = 2.0025, $a_{\alpha H}$ (triplet) = 23.31 G, $a_{\beta H}$ (triplet) = 33.93 G at −100°] are comparable to other β-fluoroalkyl radicals in Table II (see Supplementary Material). Thus, the esr parameters clearly show that the adduct cannot have the isomeric structure IVb.

In order to verify this unexpected observation, we added *tert*-butyl hypochlorite to vinylidene fluoride in cyclopropane solutions at 0° under irradiation with visible light. The 1:1 adduct VIa was isolated by preparative gas chromatography as a single isomer. A cyclopropane solution of VIa and triethylsilyl radicals generated from triethylsilane afforded an esr spectrum shown in Figure 5 which is the same as that of Va produced from di-*tert*-butyl peroxide and vinylidene fluoride.



$$(CH_3)_3COCl + CH_2{=}CF_2 \rightarrow \begin{cases} (CH_3)_3COCF_2CH_2Cl & \\ \text{VIa} & (20a) \\ (CH_3)_3COCH_2CF_2Cl & \\ \text{VIb} & (20b) \end{cases}$$

$$(CH_3)_3COCF_2CH_2Cl + Et_3Si\cdot \longrightarrow (CH_3)_3COCF_2CH_2\cdot + Et_3SiCl \qquad (21)$$

The structures of adducts VIa and VIb from the reaction of the *tert*-butyl hypochlorite and vinylidene fluoride are not readily distinguished by their pmr spectra. Instead, VIa was hydrolytically degraded to chloroacetic acid which was then converted *in situ* to the ethyl ester in more than 70%

$$(CH_3)_3COCF_2CH_2Cl + H_2O \xrightarrow{H_3O^+} ClCH_2CO_2H \xrightarrow[EtOH]{H_3O^+} ClCH_2CO_2Et \qquad (22)$$

overall yield. Barring an unprecedented rearrangement during hydrolysis, the isomeric adduct VIb would not yield chloroacetate, and the adduct of *tert*-butyl hypochlorite to vinylidene fluoride has structure VIa.

II. Vinyl fluoride is also prone to radical addition. Photolysis of bis(trifluoromethyl) peroxide in vinyl fluoride solutions gave the well-resolved spectrum of VII.[23] Similarly,

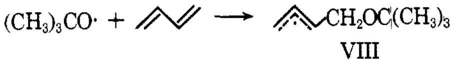
$$CF_3OOCF_3 + CH_2{=}CHF \xrightarrow{h\nu} \underset{\text{VII}}{CF_3OCH_2\dot{C}HF} \qquad (23)$$

the photolysis of di-*tert*-butyl peroxide afforded a weak spectrum of an adduct radical which we assign as VIIa on

$$(CH_3)_3COOC(CH_3)_3 + CH_2{=}CHF \xrightarrow{h\nu} \underset{\text{VIIa}}{(CH_3)_3COCH_2\dot{C}HF} \qquad (24)$$

the basis of a comparison of the esr parameters listed in Table III for analogous radicals (see Supplementary Material).

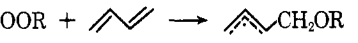
Addition of Alkoxy Radicals to Butadiene. *tert*-Butoxy radicals were shown previously to add readily to the s-trans conformer of 1,3-butadiene to generate only substituted *trans*-butenyl radicals VIII.[7] The adduct VIII is configurationally stable and easily distinguished from the isomeric cis species by the characteristic values of the hyperfine splittings for the vinylic protons.



(25)

VIII

Photolysis of *sec*-butyl, *n*-butyl, isopropyl, and *n*-propyl peroxides in the presence of 1,3-butadiene as solvent gave a well-resolved spectra of analogous alkoxy adducts IX. All the alkoxy adducts to butadiene listed in Table IV (see Supplementary Material) have comparable values for the hyperfine splittings and are easily related to the alkyl analogs, *trans*-2-buten-1-yl and *trans*-2-hexen-1-yl radicals.[7,25]



(26)

IX

$R = 1\text{-}, 2\text{-}C_4H_9;\ 1\text{-}, 2\text{-}C_3H_7$

When solutions of the tertiary and secondary alkyl peroxides with 1,3-butadiene were diluted with cyclopropane, the spectra remained the same, but only their intensity was diminished. Primary alkyl peroxides with *n*-butyl and *n*-propyl groups, however, showed unique behavior in that a different trans adduct X was formed in quite dilute solutions which has coupling constants similar to those of the alkoxy adduct. At intermediate dilutions both species IX and X were present, but the overlapping spectra gave the appearance of broadened lines which were not sufficiently well resolved for positive identification. We tentatively assign the spectra of species X to adducts derived from acyl radicals generated in the induced decomposition of primary alkyl peroxides as discussed in eq 8 above.

Discussion

Photolysis of dialkyl peroxides containing primary, secondary, and tertiary alkyl groups afford alkoxy radicals which can all be trapped by 1,3-butadiene, and the resulting allylic adduct IX can be observed by esr. However, addition of alkoxy radicals to simple alkenes depends on the structure of the alkyl group. Addition of primary or secondary alkoxy radicals to ethylene, thus, is not sufficiently rapid to compete with the facile induced decompositions of primary and secondary alkyl peroxides given in eq 8 and 9, respectively, and the esr spectra of adducts I are not observed.

Methyl peroxides are not as susceptible as primary and secondary alkyl peroxides to induced decomposition, and the esr spectrum of the methoxy adduct Ic to ethylene can be observed by esr during photolysis of methyl *tert*-butyl peroxide in eq 3. The spectrum of adduct Ib of the *tert*-butoxy radical formed simultaneously during photolysis, however, is not observed. Furthermore, deliberate attempts to add *tert*-butoxy radicals generated unambigously from the photolysis of di-*tert*-butyl peroxide (eq 2) or *tert*-butyl peracetate (eq 10) in ethylene as solvent, also afforded no esr spectrum of adduct Ib. The absence of adduct Ib cannot be attributed to its metastability since its spectrum can be readily observed when it is generated independently by bromine atom abstraction from β-*tert*-butoxyethyl bromide in eq 5.

We conclude that our inability to observe the esr spectrum of the *tert*-butoxy adduct Ib is related to its significantly slower rate of addition to ethylene compared with methoxy and other oxy radicals including hydroxyl radical.[26] A variety of oxygen-centered radicals have been examined in their addition to ethylene, and there is available literature[5,8,9,26] on esr studies relating to the observation of oxy radical adducts. Indeed, *tert*-butoxy radical is the outstanding exception among various oxygen-centered species in its slow rate of addition to ethylene. Electronic effects of the alkyl group do not appear to be a strong factor since groups as different as hydrogen, methyl, trifluoromethyl, trimethylsilyl, and acyl qualitatively show little influence on the reactivity of alkoxy radicals in additions. The single structural feature which stands out is the steric size of the *tert*-butyl group.[27,28]

A similar pattern of reactivity of alkoxy radicals is also indicated with isobutylene in which competition exists between addition and abstraction of an allylic hydrogen, and it is reflected in the steady-state concentrations of allylic and adduct radicals III and II, respectively, according to eq 23. The ratio of second-order rate constants can be obtained for these competitive processes, but absolute rate constants for hydrogen abstraction by alkoxy radicals are unknown, and rates of addition, strictly speaking, cannot be evaluated by the data on hand.

It has been suggested, however, that activation energies of abstraction reactions correlate well with the enthalpy of the reaction according to the Evans–Polanyi relationship,[29] which implies that steric and polar effects are small compared with the strength of the bond being broken. If this assumption is valid for alkoxy radicals, the observed trend would reflect an increasing rate of addition to isobutylene in the order, *n*- or *sec*-butoxy > *tert*-butoxy radical, since the bond energies of the corresponding alcohols are more or less the same.[30]

Our esr studies also support the conclusion that isobutylene is more receptive than ethylene to addition of alkoxy radicals, which is in harmony with the importance of charge-transfer contributions in the interaction.[31] These differences among alkoxy radicals are largely absent in their addition to the more reactive butadiene and supported by kinetic studies in the gas phase which show that *tert*-butoxy and methoxy radicals add to butadiene at essentially the same rate.[32] Additions to vinylidene and vinyl fluorides, however, invoke opposed polar requirements in the olefinic component because of the presence of electronegative fluorines. Nonetheless, even electrophilic species such as trifluoromethoxy radicals readily undergo regiospecific addition to vinylidene fluoride at the methylene terminus. Stabilization of the resulting adducts IV by the α,α-difluoro groups may facilitate the addition of electrophilic radicals to vinylidene fluoride. It is surprising, therefore, to find that *tert*-butoxy radicals readily add to vinylidene fluoride at the difluoromethylene terminus to form the primary alkyl adduct Va, for which we can give no ready explanation.

Factors which control radical addition to unsaturated centers are generally considered to be (i) the strength of the bond formed, (ii) steric hindrance, (iii) polar effects, and (iv) the stability of the adduct radical. Several authors have recently pointed out the complex interplay among those factors as the nature of the radical and the olefin are varied.[24] The present esr study has focused on the principal adducts formed when alkoxy radicals are exposed to olefins, but the results cannot be easily used to delineate quantitative differences among these factors. In order to evolve a fuller comprehension of the addition process, therefore, it is clearly necessary to develop more sophisticated methods to measure absolute rates of addition to olefins at individual carbon centers.[33] Although a clear delineation of factors involved in homolytic additions must await more quantitative kinetic measurements, the esr studies have focused on the inadequacy of the present theories to provide a completely rational basis for prediction.

Experimental Section

Materials. Di-*tert*-butyl peroxide was obtained from Shell Chemical Co., repeatedly washed with water, dried over calcium chloride, passed through an activated alumina column, and redistilled at reduced pressure prior to use. **Bis(trifluoromethyl) peroxide** was obtained from PCR, Inc., and used as such. Di-*n*-butyl, di-*sec*-butyl, diisopropyl, and di-*n*-propyl peroxides were prepared by the method of Pryor, *et al.*[34] Methyl *tert*-butyl peroxide was prepared by the method described by Rust,[35] Dimethyl and bis(trifluoromethyl) disulfides were obtained from Columbia Organic Chemicals and PCR, respectively. Vinyl fluoride and vinylidene fluoride were obtained from DuPont Co. Ethylene, isobutylene, and 1,3-butadiene were from Matheson Co.

***tert*-Butyl 2-bromoethyl ether** was prepared by the acid-catalyzed addition of 2-bromoethanol to isobutylene, bp 65-67° (30 mm).

Methyl, *n*-butyl, and *tert*-butyl ethers of 2-bromo-2-methylpropanol were prepared by the addition of hydrogen bromide to the corresponding vinyl ethers.[37] Methyl 2-bromo-2-methylpropyl ether, bp 52-54° (65 mm). *n*-Butyl 2-bromo-2-methylpropyl ether, bp 44-45° (3.5 mm). *tert*-Butyl 2-bromo-2-methylpropyl ether, bp 67-69° (28 mm).

***n*-Butyl peracetate** was prepared from *n*-butyl hydroperoxide and acetyl chloride.[38,39]

Sample Preparation. Samples for esr studies were prepared on a vacuum line and thoroughly degassed using repeated freeze-pump-thaw cycles.[11] The composition of the samples and the temperature were varied in order to optimize the signal-to-noise level in the spectrum. In the experiments with isobutylene, the different peroxides were prepared with an equal amount of isobutylene as reproducibility as possible. The addition of an inert solvent such as cyclopropane generally reduced the amount of adduct observed.

Addition of *tert*-Butyl Hypochlorite to Isobutylene. *tert*-Butyl hypochlorite (0.02 mol, after careful purification and redistillation) and vinylidene fluoride (0.03 mol) were transferred *in vacuo* and diluted with 0.14 mol of cyclopropane. The mixture was sealed in a heavy-wall Pyrex tube and irradiated at 0° for 3 hr with light from a 100-W incandescent bulb. Cyclopropane and unreacted vinylidene fluoride were removed carefully by slowly warming the chilled tube to room temperature. The liquid residue (2.85 g) contained approximately 5% unreacted *tert*-butyl hypochlorite. Part of the mixture was separated by gas chromatography (15% FFAP on Chromosorb W, 6 ft) into two major components, *tert*-butyl alcohol (55%) and the 1:1 adduct VI (35%). The latter was isolated on a 6-ft Carbowax column as a colorless liquid. The proton nmr spectrum of a chloroform solution showed two resonances: a singlet at δ 1.44 and a triplet at δ 3.58 (J = 4.1 Hz) in a ratio of 9:2. A sample of the adduct (0.4 g) was treated with aqueous 15% sulfuric acid for half an hour at 75°. The pmr spectrum of the resulting solution showed the absence of the 1:1 adduct and a characteristic singlet resonance at δ 4.09 for chloroacetic acid, which on treatment with excess ethanol was converted to ethyl chloroacetate. The mixture was neutralized and extracted with ether; the extracts which were washed and the ether was removed. Pmr showed: δ 1.33 (triplet, 3 H), 3.98 (singlet, 2 H), and 4.24 (quartet, 2 H) for the methyl, ethereal methylene, and chloromethyl protons, respectively. Gas chromatography of the aqueous ethanol solution confirmed the presence of ethyl chloroacetate in approximately 80%.

Esr Measurements. The modified Varian 4502 X-band spectrometer, microwave frequency, light source, and sample tubes were described previously.[5,11] The relative amounts of abstraction *vs.* addition in the reaction of *tert*-butoxy radicals with isobutylene were measured by taking the ratios of the areas under selected esr lines for methallyl and adduct radicals after correction for their different degeneracies.[39]

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Supplementary Material Available. Tables I-IV, esr parameters, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction negatives) containing all the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-75-335.

References and Notes

(1) C. Walling and E. S. Huyser, *Org. React.*, **13**, 91 (1963); F. W. Stacey and J. F. Harris, Jr., *ibid.*, **13**, 150 (1963); G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," Macmillan, New York, N.Y., 1964.

(2) (a) P. S. Skell and K. J. Shea in "Free Radicals," Vol. II, Wiley-Interscience, New York, N.Y., 1973, Chapter 26; (b) L. Kaplan, "Bridged Free Radicals," Marcel Dekker, New York, N.Y., 1972.

(3) (a) A. Nechvatal, *Advan. Free-Radical Chem.*, **4**, 175 (1972); (b) *cf.* also J. R. Shelton and C. W. Uzelmeier, *J. Org. Chem.*, **35**, 1576 (1970).

(4) J. K. Kochi and P. J. Krusic, *Chem. Soc., Spec. Publ.*, **No. 24**, 147 (1969).

(5) D. J. Edge and J. K. Kochi, *J. Amer. Chem. Soc.*, **95**, 2635 (1973).

(6) (a) C. Walling, *Pure Appl. Chem.*, **15**, 69 (1967); (b) K. U. Ingold, ref 2a, Vol. I, p 38; (c) H. Hefter, T. Hecht, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 2793 (1972).

(7) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **90**, 7157 (1968).

(8) K. S. Chen and J. K. Kochi, *J. Amer. Chem. Soc.*, **96**, 1383 (1974).

(9) D. J. Edge and J. K. Kochi, *J. Chem. Soc., Perkin Trans. 2*, 182 (1973).

(10) M. C. R. Symons, *J. Amer. Chem. Soc.*, **91**, 5924 (1969).

(11) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971).

(12) C. J. Michejda, R. J. Buenker, S. D. Peyerimhoff, and S. Shih, 166th National Meeting of the American Chemical Society, Chicago, Ill., Abstract ORGN-16; see also *J. Amer. Chem. Soc.*, **94**, 7620 (1972); C. J. Michejda and D. H. Campbell, *ibid.*, **96**, 929 (1974).

(13) The minor lines in the spectrum ($a_{\mathrm{CH_2}}$ = 17.98 G, a_{OH} = 1.63 G, $\langle g \rangle$ = 2.00327) are due to the hydroxymethyl radical derived from methanol. The presence of the latter clearly indicates that methoxy radical formed in the photolysis is also undergoing hydrogen abstraction in competition with addition in eq 9.

(14) A. Hudson and R. A. Jackson, *J. Chem. Soc., Chem. Commun.*, 1327 (1969).

(15) Chemical studies show that even 2-phenoxyethyl radical does not undergo β elimination [W. M. Horspool and C. Pauson, *Monatsh. Chem.*, **98**, 1256 (1967)].

(16) For esr spectra of acyl radicals from photolysis of ketones, see H. Paul and H. Fischer, *Helv. Chim. Acta*, **56**, 1575 (1973).

(17) R. Hiatt in "Organic Peroxides," D. Swern, Ed., Wiley-Interscience, New York, N.Y., 1973, p 6 ff.

(18) R. Livingston and H. Zeldes, *J. Chem. Phys.*, **44**, 1245 (1966); *J. Amer. Chem. Soc.*, **88**, 4333 (1966).

(19) *Cf.* D. M. Camaioni, H. F. Walter, J. E. Jordan, and D. W. Pratt, *J. Amer. Chem. Soc.*, **95**, 7978 (1973).

(20) C. Walling and W. Thaler, *J. Amer. Chem. Soc.*, **83**, 3877 (1961).
(21) H. J. Hefter, C. S. Wu, and G. S. Hammond, *J. Amer. Chem. Soc.*, **95**, 851 (1973); S. A. Weiner and G. S. Hammond, *ibid.*, **91**, 986 (1969).
(22) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N.Y., 1969, Chapter 6.
(23) K. S. Chen, P. J. Krusic, and J. K. Kochi, *J. Phys. Chem.*, **78**, 2030 (1974).
(24) (a) D. C. Nonhebel and J. C. Walton, "Free Radical Chemistry," Cambridge, University Press, Cambridge, 1974, p 158 ff; (b) D. S. Ashton, A. F. Mackay, J. M. Tedder, D. C. Tipney, and J. C. Walton, *J. Chem. Soc., Chem. Commun.* 496 (1973).
(25) T. Kawamura, P. Meakin, and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 8065 (1972).
(26) (a) W. E. Griffiths, G. F. Longster, J. Myatt, and P. F. Todd, *J. Chem. Soc. B*, 530 (1967). (b) The rate constant for addition of $H\dot{O}$ to ethylene is in excess of 10^9 M^{-1} sec^{-1} [J. K. Thomas, *J. Phys. Chem.*, **71**, 1925 (1967); C. F. Cullis, *et al.*, *Proc. Roy. Soc., Ser. A*, **300**, 443 (1967)].
(27) However, the recent report of the addition of perfluoro-*tert*-butoxy radical to ethylene suggests that polar effects must also be considered [A. G. Davies, R. W. Dennis, B. P. Roberts, and R. C. Dobbie, *J. Chem. Soc., Chem. Commun.*, 468 (1974)].
(28) A somewhat different conclusion based on product studies has been published subsequent to the submission of this paper [C. Walling and R. T. Clark, *J. Amer. Chem. Soc.*, **96**, 4530 (1974)].
(29) Reference 24a, p 240 ff.
(30) (a) R. T. Sanderson, "Chemical Bonds and Bond Energy," Academic Press, New York, N.Y., 1971. (b) Furthermore, the electron affinities of $CH_3O\cdot$, $CH_3CH_2O\cdot$, $(CH_3)_2CHO\cdot$, and $(CH_2)_3CO\cdot$ increases in the order: 40.8, 42.7, 44.1, and 44.9 kcal mol^{-1}. $CF_3O\cdot$ probably has the highest value [private communication, Dr. P. Kebarle; *cf.* R. T. McIver, Jr., and J. S. Miller, *J. Amer. Chem. Soc.*, **96**, 4324 (1974)].
(31) Reference 24a, p 143.
(32) G. Massif and E. A. Lissi, *Ber. Bunsenges. Phys. Chem.*, **78**, 203 (1974).
(33) There are very few rate constants determined for reactions of alkoxy radicals in solution [J. A. Howard, *Advan. Free-Radical Chem.*, **4**, 66 (1972)].
(34) W. A. Pryor, D. M. Huston, T. R. Fiske, T. C. Pickering, and E. Ciuffarin, *J. Amer. Chem. Soc.*, **86**, 4237 (1964).
(35) F. F. Rust, F. H. Seubold, and W. E. Vaughan, *J. Amer. Chem. Soc.*, **72**, 338 (1950).
(36) A. J. Solo and J. O. Gardner, *J. Med. Chem.*, **14**, 222 (1971).
(37) W. T. Olson, H. P. Hipsher, C. M. Buess, I. A. Goodman, I. Hart, J. H. Lamneck, Jr., and L. C. Gibbons, *J. Amer. Chem. Soc.*, **69**, 2451 (1947).
(38) H. R. Williams and H. S. Mosher, *J. Amer. Chem. Soc.*, **76**, 2984 (1954).
(39) D. Swern, ref 17, Vol. I, 1970, p 74 ff.
(40) J. E. Wertz and J. R. Bolton, "Electron Spin Resonance," McGraw-Hill, New York, N.Y., 1972, p 33 ff.

Selective, High-Yield, Linear Dimerization of 1,3-Butadiene Catalyzed by $(PPh_3)_2NiBr_2$ and $NaBH_4$ and Its Polymer-Bound Ni(0) Analog

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Abstract: The tendency of nickel to cyclodimerize butadiene has been overcome with the catalytic system $(Ph_3P_2)NiBr_2$ + $NaBH_4$ in THF-ethanol or benzene-ethanol. The reaction gives, in high yield (95%), one specific linear product, (*E,E*)-1,3,6-octatriene. $(Ph_3P)_2NiCl_2$ gives the same product though in only 81% yield. The polymer-bound analog (**2**) also gives the same product in good yield (91%). This polymer-bound system has the advantages of both homogeneous catalysis, plus the ease of catalyst recovery of heterogeneous catalysis. Attempts to dimerize isoprene with this catalytic system were unsuccessful, as were attempts to codimerize isoprene and butadiene. In equimolar amounts, isoprene also inhibited the self-dimerization of butadiene.

Cyclic oligomerization of acetylenes[1-4] and butadiene[2-5] by Ni(0) catalysts is well known. Linear oligomerization of butadiene by Ni(0) catalysts is less common, but it has been accomplished using nickel carbonyl phosphites and phosphines, as well as bisacrylonitrile nickel and phosphites in the presence of alcohols,[6] to give 1,3,6-, 1,3,7-, and 2,4,6-octatrienes. In the presence of dialkylamines (*i.e.*, morpholine) and a nickel(0) triethylphosphite, butadiene was converted to (*E,E*)- and (*Z,E*)-1,3,6-octatriene.[7] The linear dimerization of butadiene[8] has also been catalyzed with both salts and zero valent complexes of Co and Fe to give product mixtures where 3-methyl-1,4,6-heptatriene predominates,[8] by $RhCl_3$ and particularly $(Ph_3P)_2Pd$(maleic anhydride)$_2$ to give 1,3,7-octatriene.[9,10]

Because the linear dimerization of butadiene is of commercial interest,[11] the discovery of butadiene to a single linear dimer in high yield is an important goal. Furthermore, selective catalysts which are easy to handle, readily recycled, and inexpensive are needed. Thus, research on butadiene oligomerization continues to appear. Bis(triphenylphosphine)(*p*-benzoquinone)palladium, for example, produces linear dimers with 4-vinylcyclohexene as a by-product.[12] High yields of octatrienes were also obtained from butadiene over $(PPh_3)_3Pt$ under 400 psi of carbon dioxide, but in the absence of carbon dioxide, 4-vinylcyclohexene was formed in 90-97%.[12] Similar results were obtained with $(PPh_3)_4Pd$.[13,14] With bis(π-allyl)palladium, linear trimers (*n*-dodecatetraene) and higher oligomers are formed, while bis(π-allyl)nickel converts butadiene to cyclododecatriene, and bis(π-allyl)platinum gives trimer and tetramer mixtures at higher temperatures.[15] When triphenylphosphine is added to π-allylpalladium acetate, linear dimerization predominates.[16] Gardner and Wright[17] have reported that an 80% yield of octa-1,7-diene can be obtained when platinum salts, such as $LiPtCl_4$, were used in formic acid-dimethylformamide.

Features common to most catalytic systems capable of butadiene oligomerization are (1) their dependence on solvent and (2) their tendency to give product mixtures. Recently, Beger, *et al.*,[18] showed that the oligomerization of butadiene over nickel chloride or nickel acetylacetonate, in the presence of butyllithium and PL_3 (L = NMe_2, *n*-Bu, Ph, or *n*-BuO), gave complex mixtures of octatrienes and both monomeric and dimeric ethers when ethanol was present. Similarly, a bis(triphenylphosphine)nickel catalyst, produced *in situ* by the reduction of $(Ph_3P)_2NiBr_2$ with $NaBH_4$ in ethanol, catalyzed dimerization of butadiene to a mixture of linear and cyclic products.[19] When the $NaBH_4$/Ni ratio was 1 or less, the main product was 2-methylenevinylcyclopentane. When this ratio exceeded 1, linear dim-