and then partitioned between $CHCl_3$ and H_2O. The organic solution was dried over Na_2CO_3 and concentrated to leave 126 mg of the crude hydroxy ether **19b** as a colorless liquid: ir (CCl_4) 3470 (OH) and 1735 cm^{-1} (ester C=O); nmr (CCl_4) prominent singlets at δ 3.59 (CH_3O) and 2.23 (aryl CH_3) attributable to the ether **19b**. To a solution of the crude hydroxy ether **19b** (126 mg) in 2 ml of CH_2Cl_2 was added a solution of 704 mg (2.73 mmol) of $CrO_3(pyridine)_2$ in 7 ml of CH_2Cl_2. The resulting red-brown solution was stirred at 25° for 1 hr and then partitioned between Et_2O and aqueous 5% NaOH. The organic layer was washed with H_2O, dried over Na_2CO_3, and concentrated. Chromatography of the residual yellow liquid (101 mg) on silica gel with Et_2O–hexane (1:3, v/v) separated 52 mg (66% based on the hydroxy acetate **5b**) of early fractions containing (tlc and ir analysis) the keto ether **20** as a colorless liquid: ir (CCl_4) 1765 (C=O in a five-membered ring) and 1735 cm^{-1} (ester C=O); nmr (CCl_4) δ 6.8–7.3 (3 H m, aryl CH), 4.5–5.1 (1 H m, OCHO), 3.3–3.8 (*ca.* 7 H m, CH_2O, two benzylic CH with a singlet at δ 3.74, and a CH_3O singlet at 3.61), and 1.1–2.6 (*ca.* 17 H m, aliphatic CH including an aryl CH_3 singlet at δ 2.26). Later fractions from the chromatography contained (tlc and ir analysis) a second component believed to be the isomeric hydroxy ether **22b**.

A 0.19 *M* solution of "salt-free" $Ph_3P=CH_2$ in benzene was prepared from $NaNH_2$ and $Ph_3PCH_3^+Br^-$ by the procedure of Schlosser and coworkers.[12] A solution of 52 mg (0.14 mmol) of the keto ether **20** in 0.5 ml of anhydrous PhH was treated with 0.86 ml of the PhH solution containing 0.16 mmol of $Ph_3P=CH_2$. After the resulting yellow solution had been refluxed for 6 hr, it was cooled, treated with 0.5 ml of aqueous 1 *M* HCl, and then partitioned between $CHCl_3$ and H_2O. The organic solution was dried and concentrated and a solution of the residual yellow oil (104 mg) in 1.0 ml of THF was treated with 0.5 ml of aqueous 1 *M* HCl and then stirred at 25° for 1 hr. The resulting mixture was again partitioned between $CHCl_3$ and H_2O and the organic layer was dried, concentrated, and chromatographed on silica gel. The early fractions, eluted with Et_2O–hexane (1:3 v/v), contained 29 mg (72%) of the hydroxy olefin **21** as a viscous, colorless liquid. This product was shown to have the same structure as the methyl (+)-epiallogibberate (**12a**) by comparison of ir (CCl_4), uv (95% EtOH), nmr ($CDCl_3$), and mass spectra and tlc R_f values (silica gel coating). The later fractions from the chromatograph, eluted with Et_2O, contained 32 mg (85%) of crystalline Ph_3PO, mp 154–156°.

A solution of 53 mg (0.18 mmol) of the hydroxy ester **21** and 1.0 ml of aqueous 4 *M* NaOH in 1.0 ml of MeOH was refluxed for 1 hr and then partitioned between $CHCl_3$ and aqueous 5% NaOH. The aqueous layer was acidified (HCl) to pH 1 and extracted with EtOAc. After the EtOAc extract had been washed with H_2O, dried, and concentrated, the white solid residue (53 mg) was recrystallized from MeOH–Et_2O to separate 40 mg (80%) of racemic epiallogibberic acid (**3**) as white prisms, mp 253–255° dec. Recrystallization from MeOH sharpened the decomposition point to 254–255.5° dec.

Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.18; H, 7.11.

This product was shown to have the same structure as a sample of (+)-epiallogibberic acid by comparison of mass spectra, nmr spectra [$(CD_3)_2NCDO$], uv spectra (95% EtOH), and ir spectra ($CHCl_3$ containing 5% Et_3N).

Registry No.—**1**, 77-06-5; (±)-**3**, 28862-60-4; (+)-**3**, 13613-87-1; **4a**, 37741-45-0; **4b**, 38223-11-9; **5a**, 38229-34-4; **5b**, 38229-35-5; **5c**, 38229-36-6; **8a**, 38229-37-7; **8b**, 38229-38-8; **12a**, 34707-34-1; **12b**, 38229-40-2; **12c**, 38229-41-3; **13a**, 38229-42-4; **14a**, 38229-43-5; **14b**, 38229-44-6; **15**, 38229-45-7; **16a**, 38229-46-8; **16b**, 38229-47-9; **18**, 38229-48-0; **19a**, 38229-49-1; **19b**, 38229-50-4; **20**, 38229-51-5; **21**, 38229-52-6.

Reactivities of Polystyrene and Polypropylene toward *tert*-Butoxy Radical

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Di-*tert*-butylperoxy oxalate was decomposed at 45° under vacuum in benzene solutions of polystyrene, polypropylene, and several aromatic and aliphatic hydrocarbons. The relative reactivities of the substrates and the carbon–hydrogen bonds were measured from the ratio of *tert*-butyl alcohol and acetone formed. Both polymers were found to be less reactive than the corresponding simple model hydrocarbons: polypropylene was about one-half as reactive as calculated from 2,4-dimethylpentane and 2,2,4-trimethylpentane, and polystyrene was about one-fifth as reactive as polypropylene.

The autoxidation of polyolefins must proceed by a radical chain mechanism[1] similar to simple hydrocarbons, where hydrogen atom abstractions from the substrate by the peroxy and alkoxy radicals are among the important rate-determining steps.[2]

$$RH + ROO\cdot \longrightarrow R\cdot + ROOH$$

$$RH + RO\cdot \longrightarrow R\cdot + ROH$$

The reactivities of various hydrocarbons toward peroxy[3,4] and alkoxy[5] radicals have been determined by several investigators. Especially, those for *tert*-butoxy radical have been most extensively studied partly because the *tert*-butoxy radical can be produced rather easily from di-*tert*-butyl peroxide,[6] *tert*-butyl hypohalite,[5] di-*tert*-butylperoxy oxalate (DBPO),[7] and *tert*-butyl hyponitrite.[8]

To our knowledge, however, the reactivities of polyolefins toward the radicals have not yet been obtained. In the course of our study on the autoxidations of polyolefins, we measured the reactivities of the polymers toward oxy radicals. The objective of this work is to determine the relative reactivities of polystyrene and polypropylene toward *tert*-butoxy radical and to compare them with the simple, corresponding model hydrocarbons.

Experimental Section

Materials.—Polypropylene, kindly supplied by Mitsui Petrochemical Industries, was first soaked in benzene at room tem-

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perature for about 1 week. The insoluble fraction was separated by filtration. The soluble fraction was repeatedly precipitated from benzene solution by adding into excess methanol. It was finally dried *in vacuo* at room temperature. The intrinsic viscosity of the polypropylene determined at 45° in benzene was 0.180, and the number average molecular weight calculated by the following equation[9] was 9500.

$$[\eta] = 2.70 \times 10^{-4} M_n^{0.71}$$

The infrared spectrum of the purified polypropylene showed little absorption at 997 cm^{-1} but strong absorption at 975 cm^{-1}, indicating that little isotactic polypropylene was present.

Commercial polystyrene was purified like polypropylene using benzene and methanol as solvent and precipitant, respectively. The polystyrene solution was then washed successively with acid, water, alkali, and water. Finally its 2% solution of chloroform was introduced slowly into excess methanol while vigorously stirring to obtain white powder polystyrene. The purified polystyrene completely dissolved in methyl ethyl ketone, indicating that it is all atactic. The intrinsic viscosity of the polystyrene measured in benzene at 45° was 0.825, the calculated[10] number average molecular weight being 190,000.

$$[\eta] = 2.7 \times 10^{-4} M_n^{0.66}$$

The hydrocarbons were purified by conventional methods. The purities were higher than 99%. Di-*tert*-butylperoxy oxalate was prepared by the method of Bartlett, *et al.*[7]

Procedures.—Dried DBPO was weighed into the appropriate solution of substrate and benzene prepared beforehand. The aliquot of the solution (usually 0.5 ml) was taken into a 10-mm o.d. ampoule, which was degassed and sealed under vacuum (10^{-6} Torr). The tube was immersed into a water bath maintained at 45°, and DBPO was allowed to decompose completely in about its 10 half-lives. The half-life of DBPO at 45° was measured in several media, including viscous polymer solution, by following the rate of carbon dioxide evolution using a Toepler pump and it was obtained as 41 min, which is in good agreement with the previously reported value of 42 min in benzene solution.[7] After the decomposition, the ampoule was opened, internal standard was added by syringe, and the mixture was analyzed with glc equipped with digital integrator using a 3 mm × 7 m Carbowax 20M column. The temperature of the injection port and the column was kept below 90° to avoid the thermal decomposition of di-*tert*-butyl peroxide in glc. When the reaction mixture was too viscous to syringe directly, the ampoule was connected to the vacuum line and the volatile products and the internal standard were transferred first below 0° and finally at 50° into a trap cooled with liquid nitrogen under vacuum.

More than one run was performed in many of the solutions and the reproducibility was better than 5%. In order to minimize the effect of experimental error, k_a/k_d ratios were determined graphically from several runs rather than from one point measurement (see text).

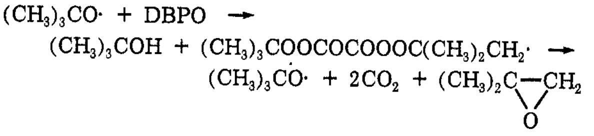
Results and Discussion

On thermal decomposition, each molecule of DBPO quantitatively yields two *tert*-butoxy radicals and two molecules of carbon dioxide. The caged pair of *tert*-butoxy radicals either recombines to give di-*tert*-butyl peroxide ($t\text{-}Bu_2O_2$) or diffuses apart. The free *tert*-butoxy radicals may either abstract hydrogen from the substrate to give *tert*-butyl alcohol or may cleave to yield acetone and methyl radical.

$$(CH_3)_3CO\cdot + RH \xrightarrow{k_a} (CH_3)_3COH + R\cdot \qquad (1)$$

$$(CH_3)_3CO\cdot \xrightarrow{k_d} CH_3COCH_3 + CH_3\cdot \qquad (2)$$

Quite a small amount of isobutylene oxide was observed among the products, which must arise by the attack of *tert*-butoxy radical on the terminal hydrogen of DBPO and subsequent scission of the radical formed from DBPO.



$$(CH_3)_3CO\cdot + DBPO \rightarrow (CH_3)_3COH + (CH_3)_3COOCOCOOOC(CH_3)_2CH_2\cdot \rightarrow (CH_3)_3CO\cdot + 2CO_2 + (CH_3)_2C\overset{O}{—}CH_2 \qquad (3)$$

The methyl radical produced in reaction 2 presumably reacts with the substrate to yield methane and alkyl radical. The alkyl radicals are assumed to give a dimer by combination or a parent substrate and olefin by disproportionation. Under these circumstances, the relative reactivities of various hydrocarbons can be measured indirectly[11] by measuring the amount of *tert*-butyl alcohol, isobutylene oxide, and acetone formed. The *tert*-butyl alcohol produced in reaction 3 is corrected.

$$\frac{[t\text{-BuOH}]}{[Me_2CO]} = \frac{k_a[RH]}{k_d} \qquad (4)$$

The measurement of the substrate reactivities by the direct method[11] by following the competitive disappearance of the substrates themselves was not employed, since in this system the parent hydrocarbons are reproduced from the corresponding radical by disproportionation and the substrate may also be attacked by methyl radical formed in reaction 2.

Results of the decomposition of DBPO in benzene with added aromatic compounds and polystyrene are summarized in Table I. In neat benzene, only 88.6% of the initial *tert*-butoxy group could be accounted for. Extensive efforts were not devoted to find the missing *tert*-butoxy group, but this may be bound to the aromatic ring as, for example, *tert*-butyl phenyl ether. The amount of missing *tert*-butoxy group decreased in general with increasing concentration of the hydrogen donor. In polystyrene–benzene media, considerable *tert*-butoxy group was always unaccounted for. They may be bound to the polymer chain as *tert*-butyl ether, as was found in the decomposition of DBPO in bulk polypropylene.[1]

TABLE I

DECOMPOSITION OF DBPO IN BENZENE SOLUTION AT 45°

Substrate, RH	[RH], *M*	Products,[a] % of *t*-BuO: $t\text{-}Bu_2O_2$	Me_2CO	*t*-BuOH	*t*-BuO accounted for, %
Neat benzene		4.5	40.0	43.8	88.6
tert-Butylbenzene	1.08	5.3	31.2	60.3	97.0
tert-Butylbenzene	1.62	5.2	24.0	64.0	93.4
tert-Butylbenzene	3.23	7.9	14.8	72.5	95.2
tert-Amylbenzene	0.98	5.8	20.8	68.0	94.6
tert-Amylbenzene	1.47	6.1	16.4	74.4	96.9
tert-Amylbenzene	1.96	6.1	12.5	76.9	95.5
Cumene	0.60	5.4	11.6	76.8	93.8
Cumene	0.90	5.7	8.9	82.1	96.7
Cumene	1.44	6.4	5.4	88.7	100
Cumene	1.80	5.8	4.5	90.8	101
Polystyrene[b]	0.175	4.2	38.4	43.3	85.9
Polystyrene	0.341	4.5	40.3	46.9	92.1
Polystyrene	0.803	4.6	35.2	43.6	84.1
Polystyrene	1.356	5.1	35.7	48.0	88.8
Polystyrene	1.448	4.2	34.4	47.0	85.5

[a] [DBPO] = 0.1 *M*; 0.1–0.3% of isobutylene oxide was also found. [b] Concentrations are in monomer units.

Figure 1 shows the plots of the *tert*-butyl alcohol/acetone ratio as a function of the substrate concentration. Satisfactory straight lines are obtained and the

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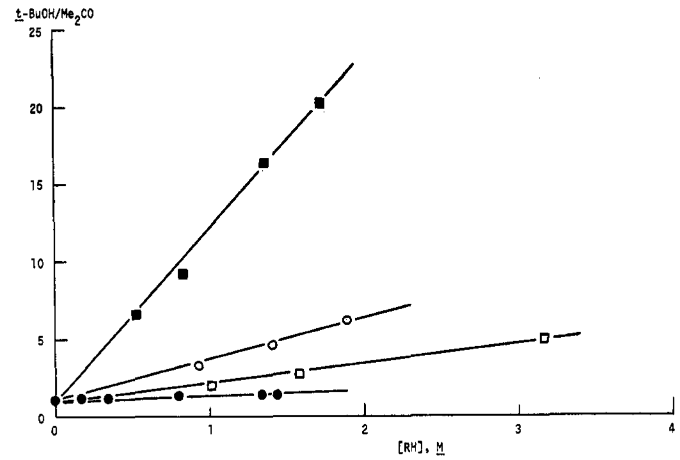

Figure 1.—Decomposition of DBPO at 45° in benzene solution of cumene (■), *tert*-amylbenzene (○), *tert*-butylbenzene (□), and polystyrene (●).

calculated k_a/k_d values from the slope are summarized in Table II. It shows that cumene is 7.1 times as reactive as *tert*-butylbenzene, which agrees well with the value of 7.3 obtained by Walling and Jacknow[5] at 40° using *tert*-butyl hypochlorite.

TABLE II
RELATIVE RATES OF HYDROGEN ABSTRACTION BY *tert*-BUTOXY RADICAL AT 45°

Substrate	k_a/k_d per molecule	Relative k_a per hydrogen
Benzene	0.098	Aromatic, 1
tert-Butylbenzene	1.40	Primary, 10.7
tert-Amylbenzene	3.07	Secondary, 54.1
Cumene	11.46	Tertiary benzylic, 656
Polystyrene	0.186	

Solvent effects on the k_a/k_d ratio have been observed and it is reported that olefinic and polar solvents give a higher value for k_d while the hydrogen atom abstraction is relatively solvent insensitive.[12] However, k_d may be assumed to be virtually constant for the present system of nonpolar aromatic hydrocarbons in excess benzene solvent. The calculated relative reactivities of the various types of carbon–hydrogen bonds are also summarized in Table II.[13] It is quite surprising that the observed k_a/k_d for polystyrene is only 0.186, 1.5% of the calculated value of 12.3.

Figure 2 shows the plots of the *tert*-butyl alcohol/acetone ratio as a function of substrate concentrations in the decomposition of DBPO in benzene solutions of polypropylene and several aliphatic hydrocarbons. More than 90% of the initial *tert*-butoxy group was always accounted for in each experiment, with less missing *tert*-butoxy group with increasing concentrations of the substrate. The calculated k_a/k_d values are summarized in Table III. Assuming that k_d is virtually constant in the present system, the relative reactivities of carbon–hydrogen bonds were calculated. The relative reactivities of the primary, secondary, and tertiary carbon–hydrogen bonds were calculated from the data for pentane, hexane, heptane, and 2,3-dimethylbutane. In Table III are also shown the values relative to aromatic hydrogen, and it gives the relative reactivity series of 1:6.9:20 for primary, secondary, and tertiary aliphatic hydrogens This is only in fair agreement with the relative reactivities of 1:10:44 obtained by Walling and Jacknow[5] at 40° for butane and 2,3-dimethylbutane. However, since the reactivity of the primary hydrogen is obtained as a small difference between large quantities, a small experimental error will produce quite a large error in the relative reactivity series. In fact, if the relative reactivities of primary, secondary, and tertiary hydrogens are 1:5:20, the relative reactivities of pentane, hexane, heptane, and 2,3-dimethylbutane are 1:1.28:1.56:1.44, whereas, if the relative reactivities of hydrogens are 1:10:40 instead, the relative reactivities of these four compounds change to 1:1.30:1.61:1.39. Thus, the relative reactivities of hydrogens change drastically with a small change in the reactivities of the substrates.

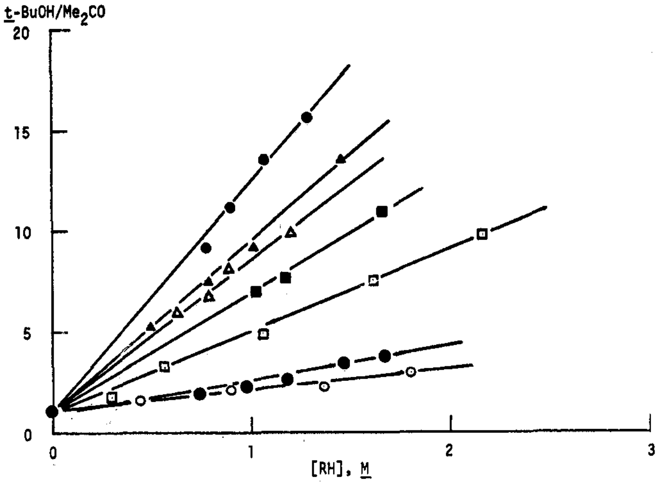

Figure 2.—Decompositions of DBPO at 45° in benzene solutions of heptane (◎), hexane (▲), 2,3-dimethylbutane (△), pentane (■), 2,4-dimethylpentane (□), 2,2,4-trimethylpentane (●), and polypropylene (⊙).

TABLE III
RELATIVE RATES OF HYDROGEN ABSTRACTION BY *tert*-BUTOXY RADICAL AT 45°

Substrate	k_a/k_d per molecule	Relative k_a per hydrogen
Benzene	0.098	Aromatic, 1
Pentane	6.68	Primary, 8.75
Hexane	8.50	Secondary, 60.6
Heptane	10.54	Tertiary, 176
2,3-Dimethylbutane	7.29	
2,4-Dimethylpentane	4.30	
2,2,4-Trimethylpentane	2.13	
Polypropylene	0.98	

The k_a/k_d ratios for 2,4-dimethylpentane and 2,2,4-trimethylpentane, relevant model compounds for polypropylene, calculated with the values in Table III are 9.24 and 6.85, respectively. Thus, the observed reactivities of 2,4-dimethylpentane and 2,2,4-trimethylpentane are about one-third to one-half the calculated reactivities. The low reactivities of these compounds toward *tert*-butoxy radical have been already reported

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(12) C. Walling and P. Wagner, *J. Amer. Chem. Soc.*, **86**, 3368 (1964); C. Walling, International Symposium on Free Radicals in Solution, Michigan, Aug 1966.

(13) The data in Table II would be more useful if the contribution from aromatic abstraction were ignored in calculating k_a/H, since the removal of an aromatic hydrogen may not be direct abstraction but probably addition–abstraction and has little relationship to the other k_a's. On this basis, the relative k_a per hydrogen for primary, secondary, and tertiary benzylic hydrogens in Table II is 1:5.4:68. However, the k_a values are given relative to aromatic hydrogen so as to compare directly the primary and secondary hydrogens of aromatic and aliphatic hydrocarbons.

by Brook[14] and these have been also observed for phenyl,[15] nitrophenyl,[16] and methyl[17] radicals and hydrogen atom.[18] This is explained as being due to the preferred conformation of the substrates.[14,15,17]

The observed reactivity of polypropylene is only about 20% of the calculated reactivity from the values in Table III. Considering the structure and numbers of the primary, secondary, and tertiary hydrogens, the reactivity of polypropylene is expected to be about one-half of that of 2,4-dimethylpentane and roughly the same as that of 2,2,4-trimethylpentane. Table III indicates, however, that toward *tert*-butoxy radical polypropylene is about one-half as reactive as expected from the corresponding model compounds.

Also, polystyrene is much less reactive than expected, as shown in Table II. Metz and Mesrobian[19] suggested that the low oxidizability of polystyrene was due to the steric hindrance and steric inhibition of resonance for the attack of peroxy radical on polystyrene. As they pointed out, if the phenyl groups on alternating carbon atoms are out of plane of the polymer chain owing to their close proximity to each other, benzyl resonance (as large as 13 kcal/mol[20]) cannot occur. However, if this is the sole reason for its low reactivity, polystyrene should be at least as reactive as *tert*-amylbenzene. Table II shows that polystyrene is only $^1/_{16}$ as reactive as *tert*-amylbenzene.

The following argument shows that the polar effect is unimportant. It is known that aliphatic secondary hydrogens are more reactive than the benzylic hydrogen of toluene toward an electronegative chlorine atom (electron affinity: 3.64 eV[21]). This is explained by the inductive electron-withdrawing effect of the phenyl group. The *tert*-butoxy radical (electron affinity: 2.6 eV[22]) is also a powerful electron acceptor, preferentially attacking points of high electron availability, but not as strong as chlorine atom. Tables II and III indicate that the primary and secondary hydrogens of *tert*-butylbenzene and *tert*-amylbenzene, respectively, are about as reactive as aliphatic primary and secondary hydrogens and that benzylic hydrogen is much more reactive than the corresponding aliphatic hydrogen. Thus, the electron-withdrawing properties of the phenyl group may not be responsible for much lower reactivity of polystyrene than polypropylene.

If the reactivity of the tertiary hydrogen of polystyrene is same as that of aliphatic tertiary hydrogen, the k_a/k_d is calculated to be 5.34. Thus, the extraordinarily low reactivity of polystyrene may be ascribed mainly to the preferred conformation of the molecule: the bulky phenyl group on alternating carbon atoms must protect tertiary and also, probably, secondary hydrogens from the attack of rather bulky *tert*-butoxy radical.

However, the discussion given above does not explain why polymers are less reactive than the corresponding model compounds. One possible explanation may be that the polymers are special in having coiled configurations. Although benzene is a good solvent and polymers are expected to extend their chains in the benzene solution, only a limited fraction of the abstractable hydrogens may be exposed to the *tert*-butoxy radical.[23] The study of the effects of solvent, molecular weight, and temperature on the reactivities of polymers is now in preparation.

The preferential intramolecular propagation in the autoxidation of 2,4-dimethylpentane[24] and 2,4,6-trimethylheptane[25] may be partly because the approach of the bulky peroxy radical to the tertiary hydrogen is hindered by the methyl groups on alternating carbon atoms. This effect may be more important in the oxidations of polystyrene and polypropylene.

Registry No.—Polystyrene, 9003-53-6; polypropylene, 9003-07-0; *tert*-butoxy radical, 3141-58-0; di-*tert*-butylperoxy oxalate, 1876-22-8.

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