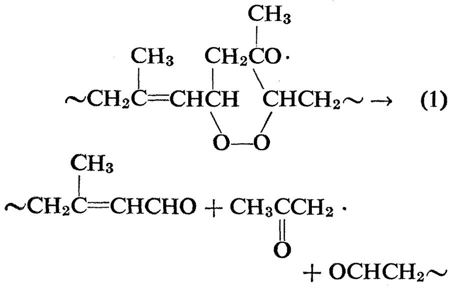
Reports

Hexanedione from Hydrocarbon Polymer Oxidation

Abstract. *The diketone 2,5-hexanedione has been isolated as a product of the thermal oxidation of* cis-*1,4-polyisoprene and of copolymers of ethylene and propylene. This is confirmatory evidence for the formation of acetonyl radicals during oxidation of these polymers and their reaction with each other in the presence of oxygen as postulated earlier.*

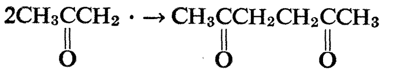
In 1959 Tobolsky and Mercurio suggested that acetonyl ($CH_3COCH_2\cdot$) radicals are produced during the oxidation of natural rubber with molecular oxygen and that these combine to form 2,5-hexanedione (*1*):



$$\begin{array}{l} \qquad\qquad\qquad\ CH_3 \\ \qquad\qquad\qquad\ \ | \\ \qquad CH_3 \quad CH_2CO\cdot \\ \qquad\ \ | \qquad\quad\ | \quad \diagdown \\ \sim CH_2C{=}CHCH \quad CHCH_2\sim\ \rightarrow \qquad (1) \\ \qquad\qquad\quad \diagdown \quad \diagup \\ \qquad\qquad\qquad O{-}O \end{array}$$

$$\sim CH_2\overset{\overset{CH_3}{|}}{C}{=}CHCHO + CH_3\underset{\underset{O}{\|}}{C}CH_2\cdot + OCHCH_2\sim$$

and



$$2CH_3\underset{\underset{O}{\|}}{C}CH_2\cdot \rightarrow CH_3\underset{\underset{O}{\|}}{C}CH_2CH_2\underset{\underset{O}{\|}}{C}CH_3 \qquad (2)$$

An early attempt to check this suggestion was unsuccessful (*2*). Levulinaldehyde is the dicarbonyl compound formed in highest yield during the uncatalyzed thermal oxidation of natural rubber; it was estimated that hexanedione was formed in yield less than 5 percent that of levulinaldehyde during oxidation in oxygen at 120°C (*2*).

Acetonyl radicals have also been postulated to be intermediates in the oxidation of polymers and copolymers of ethylene and propylene (*3*) to account for the formation of acetone.

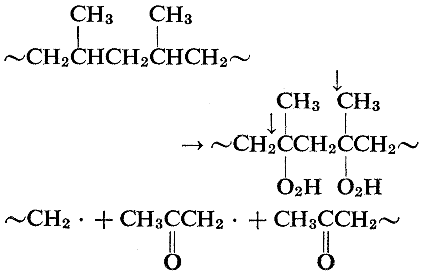
We now find that hexanedione is a product of the oxidation of both *cis*-1,4-polyisoprene (*4*) and ethylene propylene copolymers containing 40 to 50 percent combined propylene, with molecular oxygen, at temperatures higher than used previously. The yield from natural rubber is raised to 5 to 10 percent of that of levulinaldehyde when the temperature of oxidation is 150° to 180°C. Precise estimation of the relative yield is difficult with the fractionation procedures available (*5, 6*).

Apparatus, polymers, and procedures have been described (*6–8*). Samples were oxidized at atmospheric pressure in oxygen, with oven temperatures between 150° and 180°C. Volatile products were condensed in a trap at −80°C. Condensate collected in the trap in successive runs was combined and stored frozen in dry ice until sufficient material was collected. Preliminary fractionation of 0.75 g of condensate was done on 0.6 cm × 3 m chromatographic columns packed with 10 percent (by weight) of Pluronic 84 (*9*) supported on Haloport F (*9*). The fraction containing hexanedione (*7*, peak 18, Fig. 1) was collected in ether; that from several runs was combined and refractionated (*5*) on a column of 10 percent silicone fluid XF 1150 (*9*) supported on Haloport F.

For identification, hexanedione was compared with authentic material for retention time on two substrates, infrared spectrum, iodoform reaction, and x-ray diffraction patterns of the 2,4-dinitrophenylhydrazone and of the semicarbazone.

The carbon-skeleton structure represented by 2,5-hexanedione is not present in 1,4-polyisoprene. Infrared spectra of copolymers of ethylene and propylene have been interpreted as showing that tail-to-tail addition of propylene occurs (*10*); but the fraction of methyl groups separated by four chain atoms is small, and there is no reason to expect preferential attack at 1,4-substituted sites in the saturated polymers. The most reasonable explanation for the formation of hexanedione from these dissimilar polymers, therefore, appears to be the hypothesis of Tobolsky and Mercurio.

Acetonyl radicals may be formed from intermediates produced by intramolecular attack by radicals in both polymers. In natural and synthetic polyisoprene the intermediate is a cyclic peroxide as formulated in Eq. 1 (*11*). In copolymers of ethylene and propylene the intermediate is formed by the mechanism suggested by Barusch and coworkers (*12*), as indicated schematically in Eq. 3.



$$\sim CH_2\overset{\overset{CH_3}{|}}{C}HCH_2\overset{\overset{CH_3}{|}}{C}HCH_2\sim$$

$$\rightarrow \sim CH_2\!\downarrow\!\underset{\underset{O_2H}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_2\underset{\underset{O_2H}{|}}{\overset{\overset{\overset{\downarrow}{CH_3}}{|}}{C}}CH_2\sim\ \rightarrow$$

$$\sim CH_2\cdot + CH_3\underset{\underset{O}{\|}}{C}CH_2\cdot + CH_3\underset{\underset{O}{\|}}{C}CH_2\sim \qquad (3)$$

Successive breaking of carbon-to-carbon bonds, as indicated by the arrows, leads to an acetonyl radical.

The evidence for the formation and subsequent reaction of acetonyl radicals with hydrocarbon and with each other in the presence of oxygen requires reexamination of the widely made assumption that the principal fate of hydrocarbon radicals at moderate temperatures and relatively low pressures is reaction with oxygen (*13*). It is true that under our conditions, rates of oxidation of the ethylene propylene copolymers and possibly of the polyisoprene were diffusion-controlled (*14*). However, the rate of uncatalyzed oxidation of natural rubber is pressure sensitive up to at least atmospheric pressure under conditions where diffusion control is unlikely (*8*), and the rate of oxidation of simple, relatively unreactive, olefins is pressure-dependent up to several atmospheres at 120°C (*15*). The dependency implies that the concentration of hydrocarbon radicals is not negligible relative to that of peroxy radicals at pressures near atmospheric.

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Particle Size Fractionation of Airborne Gamma-Emitting Radionuclides by Graded Filters

Abstract. *Three filters in series were employed to separate into groups, according to size, the nuclear debris suspended in air at ground level. The concentrations of airborne* Ce^{144}-Pr^{144}, Sb^{125}, Cs^{137}, Zr^{95}-Nb^{95}, Mn^{54}, *and* Ru^{106}-Rh^{106} *in each size group were determined by gamma spectral analysis. Particles having diameters of less than 1.75 microns contained a minimum of 88 percent of the total activity.*

The particle size distribution of airborne radioactivity is important because it influences the rates of sedimentation, of removal from the atmosphere by precipitation, and of ground deposition of fallout. By determining the concentration of individual radionuclides in fractions of specific particle size the physical factors operative in isotopic fractionation and in the transport of nuclear debris in the atmosphere can be elucidated. Furthermore, knowledge of the particle size distribution of airborne radionuclides is pertinent to the estimation of the inhalation hazard because retention of particulate material in the lungs is not a sole function of the quantity inhaled, but also varies with particle size distribution, solubility, and aerodynamic properties.

In our study we used three filters of increasing retentivities, in series, to separate airborne particles into size groups. The radionuclide composition of the material retained on each filter was determined by gamma spectral analysis and the distribution calculated for each nuclide (Ce^{144}-Pr^{144}, Sb^{125}, Cs^{137}, Zr^{95}-Nb^{95}, Mn^{54}, and Ru^{106}-Rh^{106}) on the three filters.

Jet impactors and high-speed centrifugal precipitators were used in previous studies of this kind. While such devices have the advantage of separating particles on the basis of their aerodynamic properties, they tend to break up lose aggregates of particles and their low sampling rates make determination of low-levels of radioactivity impractical. Two-stage samplers with a small cyclone separator to remove nonrespirable particles somewhat overcome the disadvantage of low sampling rates but risk the loss of potentially useful information on particle size. As an alternative to such techniques, it was suggested that differences in filter retentivities might provide a means for studying airborne particle size distribution (*1*). The individual radionuclides obtained on filters can be quantified by radiochemical and gamma analysis. The advantage of this technique is that it permits the collection of air samples of large volume, the determination of particle size, and the non-destructive radionuclide analysis of the collected fission products.

We used a sampling head consisting of three graded 20- by 25-cm filters (referred to as filters A, B, and C) and probes up- and down-stream of each graded filter to sample a portion of the air stream. A rotary blower provided a sampling rate of 140 liters per minute through the system. Filter media CM-245 (designated filter A) (*2*), CM-285 (designated filter B), and MSA-1106BH (designated filter C) were selected from many filters tested because of their different retentivities of airborne Zr^{95}-Nb^{95}, similar gamma-counting efficiencies, and similar glass-fiber composition. The selected filters differed from those employed in previous studies by other investigators (*3*).

To obtain the relative number of particles in a specific size range captured by each graded filter, samples collected by means of the up- and down-stream probes on type AA membrane filters (*2*) were optically sized at 100× and 430×, and at oil immersion magnification (×1000). A minimum of 150 particles, or the particles distributed over an area of 3200 μ^2, were sized; although in most cases twice the minimum number of particles were sized for each probe sample. Limitations inherent in optical microscopic examination, particularly the inability to detect particles smaller than approximately 0.3 μ, tend to shift size distributions obtained.

Table 1. Average particle size parameters. The geometric S.D. (standard deviation) is the ratio of the 84-percent diameter to the 50-percent diameter.

		Filter A		Filter B		Filter C	
Sample duration (days)	No. of samples averaged	Geometric mean diameter (μ)	Geometric S.D.	Geometric mean diameter (μ)	Geometric S.D.	Geometric mean diameter (μ)	Geometric S.D.
1	4	0.65	2.12	0.36	1.80	0.28	1.57
3	7	.87	1.83	.42	1.84	.25	1.81
5	3	.89	2.11	.48	1.77	.28	1.70

Table 2. Fraction of total radionuclide activity collected on each filter.

No. of samples averaged*	Nuclide	Filter A		Filter B		Filter C	
		Range	Average	Range	Average	Range	Average
19	Ce^{144}-Pr^{144}	0.07–0.19	0.11	0.59–0.78	0.73	0.12–0.26	0.16
18	Sb^{125}	.07– .22	.11	.58– .78	.72	.10– .25	.17
8	Cs^{137}	.08– .19	.12	.65– .80	.72	.12– .22	.16
19	Zr^{95}-Nb^{95}	.06– .20	.12	.61– .77	.72	.10– .24	.16
19	Mn^{54}	.06– .25	.11	.57– .80	.74	.08– .24	.15
19	Ru^{106}-Rh^{106}	.07– .24	.13	.57– .78	.71	.10– .23	.16

* Because of low activity in some instances, less than 19 samples were averaged.