References and Notes

(1) J. L. Hoard, *Science*, **174**, 1295 (1971); J. L. Hoard in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, Chapter 8.
(2) D. A. Buckingham, J. P. Collman, J. L. Hoard, G. Lang, L. J. Radonovich, C. A. Reed and W. T. Robinson, unpublished work.
(3) D. F. Koenig, *Acta Crystallogr.*, **18**, 663 (1965); J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *J. Am. Chem. Soc.*, **87**, 2312 (1965); J. L. Hoard, G. H. Cohen, and M. D. Glick, *ibid.*, **89**, 1992 (1967); D. M. Collins, R. Countryman, and L. J. Hoard, *ibid.*, **94**, 2066 (1972); L. J. Radonovich, A. Bloom, and L. J. Hoard, *ibid.*, **94**, 2073 (1972).
(4) The prominent exception is metaquomyoglobin, in which the ferric ion is coordinated both by the proximal histidyl imidazole and a water molecule; the iron, however, is displaced 0.4 Å out of the porphyrin plane in the direction of the histidine (T. Takano, *J. Mol. Biol.*, **110**, 537 (1977)).
(5) B. D. Olafson and W. A. Goddard III, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 1315 (1977).
(6) G. N. La Mar, G. R. Eaton, R. H. Holm, and F. A. Walker, *J. Am. Chem. Soc.*, **95**, 63 (1973); F. A. Walker and G. N. La Mar, *Ann. N.Y. Acad. Sci.*, **206**, 328 (1973); G. N. La Mar and F. A. Walker, *J. Am. Chem. Soc.*, **95**, 6950 (1973); R. V. Snyder and G. N. La Ma *ibid.*, **98**, 4419 (1976).
(7) The sum of the pyrrole-H intensity in the two detectible species is constant; so all of the iron prophyrin exists in these two species. Furthermore, although PFeBr has a different NMR trace than PFeI, addition of dimethyl sulfoxide yields the identical species $PFeL_n^+$. The optical spectra of dimethyl sulfoxide adducts of natural porphyrin complexes have also been shown to be independent of either the bromide or iodide complexes used,[8] indicating the lack of a coordinated halide ion in $PFeL_n^+X^-$.
(8) R. J. Kurland, R. G. Little, D. G. Davis, and C. Ho, *Biochemistry*, **10**, 2237 (1971).
(9) The mixed solvent was used to increase the low-temperature liquid range without causing significant aggregation of the PFeI (R. V. Snyder and G. N. La Mar, *J. Am. Chem. Soc.*, **99**, 7178 (1977)).
(10) d_{20}-PFeI was required to delete the phenyl resonance of both PFeI and $PFeL_n^+$ so that the free L peak can be integrated quantitatively.
(11) T. R. Stengle and C. H. Langford, *Coord. Chem. Rev.*, **2**, 249 (1967).
(12) A broad (~1000 Hz) signal can be detected at ~10–12 ppm below Me_4Si; however, its great width and partial overlap with solvent resonance preclude integrating it directly.
(13) Details of the calculation of the terms in eq 2 in terms of the signal areas, A, are as follows: $[L]_{free} = [L]_0(A^S_{FL}/A^S_{TP})/(A^F_{TL}/A^F_{TP})$, where $[L]_0$ is the total Me_2SO concentration, A^S_{FL} and A^S_{TP} are the free Me_2SO signal area and the total pyrrole-H signal area, respectively, under conditions of slow Me_2SO exchange (i.e., $\lesssim -60$ °C), while A^F_{TL} and A^F_{TP} are the total Me_2SO signal area and the total pyrrole-H signal area, respectively, under conditions of fast Me_2SO exchange (i.e., $\gtrsim -20$ °C). $[d_{20}\text{-}PFeL_n^+] = [P]_0 A^S_C/A^S_{TP}$, where $[P]_0$ is the total porphyrin concentration, A^S_C is the pyrrole-H signal area for d_{20}-$PFeL_n^+$, and A^S_{TP} is the total pyrrole-H signal area, both under conditions of slow Me_2SO exchange ($\lesssim -60$ °C).
(14) J. Subramanian in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, Chapter 13.
(15) Determined from broadening of free L in slow exchange.[11]
(16) J. D. Satterlee, G. N. La Mar* and T. J. Bold, *J. Am. Chem. Soc.*, **99**, 1088 (1977).
(17) T. G. Spiro and J. M. Burke, *J. Am. Chem. Soc.*, **98**, 5482 (1976).
(18) M. E. Kastner, W. R. Scheidt, T. Mashiko, and C. A. Reed, unpublished work.

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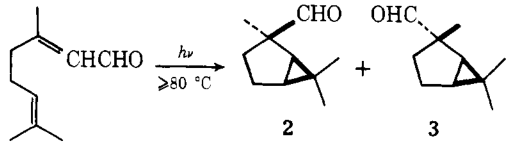
Novel Temperature-Dependent Photochemical Rearrangement of Citral

Sir:

In this report we describe the photochemical rearrangement of citral (**1**) to aldehydes **2** and **3** at elevated temperature. It



1 2 3

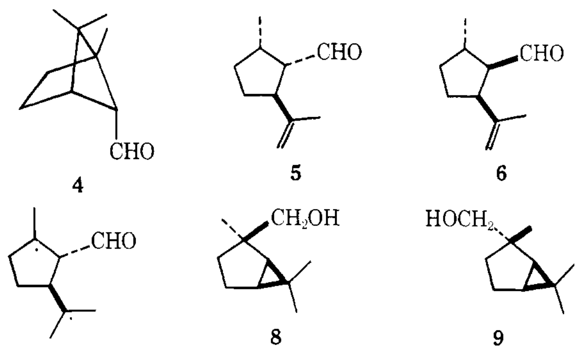
is noteworthy that these products are not seen at 30 °C but become increasingly important at higher temperatures and that their formation requires the unusual 1,2 shift of a formyl group. There have been rather few investigations of photochemical processes in solution at elevated temperature, and those reported typically concern studies below 100 °C of the kinetics or thermodynamics of processes already well known at lower temperature.[1,2] The present study, on the other hand, concerns photochemical transformations which require thermal activation beyond that available at room temperature.

Table I. Photoisomerization of Citral at Various Temperatures

Product	Yield, %				
	30 °C	80 °C	111 °C	165 °C	190 °C
2	0	4	9	26	36
3	0	1	2	7	8
4	25	23	22	15	13
5	42	40	28	16	10
6	5	6	8	6	6
Total	72	74	69	70	73

It has been known for some years that irradiation of citral (**1**) in cyclohexane or ethanol leads in moderate yield to a mixture of photocitral B (**4**) and photocitral A (**5**), and it has been suggested that these isomers may arise through coupling and disproportionation, respectively, of the biradical intermediate **7** formed on interaction of the two olefinic double bonds of **1**.[3,4] We obtained similar results in benzene at 30 °C, except that we also noted the formation of 5% of a third product later shown to be **6**. Irradiation in benzene at reflux (80 °C) gave **4–6** along with 5–10% mixture of **2** and **3**. Yield data for relatively low conversion at other temperatures are shown in Table I, in which it may be seen that at 190 °C the dominant product is **2** (36%) and the combined yield of **2** and **3** is 44%, while the total yield of volatile products remains essentially constant at ~71%.[5]

Aldehydes **4–6** were isolated and purified by preparative vapor phase chromatography (VPC) and identified through



comparison of their properties with those previously recorded.[3,4,6] A mixture of **2** and **3** was obtained similarly, but no conditions tried permitted direct separation of these products. Hydride reduction of the mixture gave alcohols **8** and **9**, which could be separated by VPC and then individually oxidized back to **2** and **3** using chromium trioxide–pyridine complex.[7] Products **2** and **3**, as well as alcohols **8** and **9**, were fully characterized; spectroscopic data[8] require the formyl group and the three methyl groups of both **2** and **3** to be on quaternary carbon atoms, indicate the absence of carbon–carbon double bonds, suggest the presence of a cyclopropane ring, and point to a close structural similarity between the two isomers. These observations, together with mechanistic considerations discussed below, led to bicyclic structures **2** and **3** for these substances. Furthermore, ^1H NMR spectra in the presence of the lanthanide shift reagent $Eu(fod)_3$[9] permitted assignment of stereochemistry as shown, since in **3** one high-field (cyclopropane methine) signal moved downfield much more rapidly than in **2**.

These conclusions were verified for the major new photoproduct **2** by independent synthesis from bishomocaronic acid

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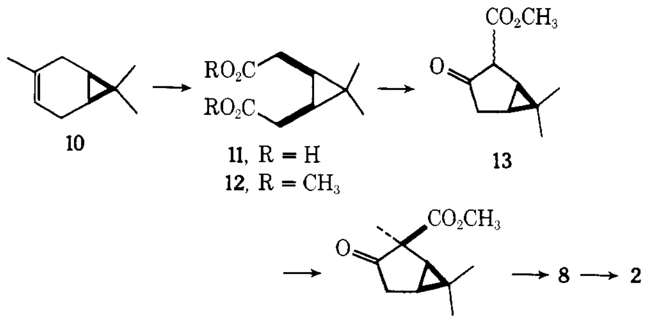


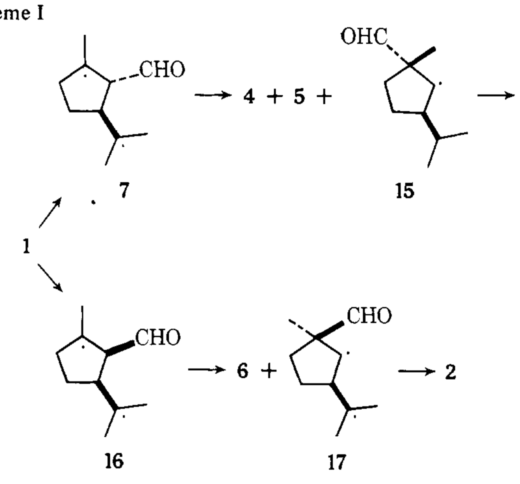
10 11, R = H 12, R = CH_3 13 14

(**11**), which is available in two steps from 3-carene (**10**).[10] The related ester **12** underwent Dieckmann cyclization[11] to furnish **13** as a mixture of epimers. Methylation of **13** using sodium hydride and methyl iodide in benzene–dimethylformamide[12] gave a single product, which is assigned the stereochemistry of **14**,[8] since the substituted cyclopropane ring effectively shields C(2) from endo approach of the methylating agent. The alkylated keto ester **14** was converted to its tosylhydrazone and then reduced with excess lithium aluminum hydride to furnish authentic **8**,[13] identical in all respects with the alcohol described above.

These photochemical rearrangements were efficiently sensitized at 30 and 132 °C by acetophenone,[14] and the products were found in the same yields and relative amounts on sensitized and direct irradiation at each temperature. Attempts to quench the reactions led to ~25% quenching at 30 °C in 2,3-dimethylbutadiene as solvent (8.85 M), with no observable effect on the ratio of products. These results suggest most simply a common triplet precursor for all products, with the lifetime of the quenchable species ~0.1 ns; other more complex interpretations are certainly possible. Experiments with purified *cis*-citral (neral) and *trans*-citral (geranial) showed that photochemical equilibration of these geometric isomers is relatively rapid, but that in the early stages of irradiation before this equilibration is complete all products are formed from each isomer and in approximately the same ratio.

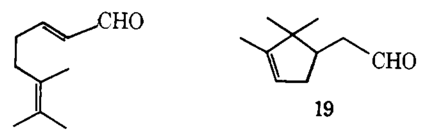
A stepwise mechanism for formation of **2** and **3** is shown in Scheme I. This is compatible with the earlier proposal[3,4] of biradical **7** as an intermediate in the reaction at room temperature and with more recent mechanistic investigations of the role of biradicals in [2 + 2] photocycloaddition.[15] It was pointed out previously that formation of **7** rather than **16** should be favored on steric grounds, and this fact was used to account for the observed stereochemistry of **4** and **5**.[4] The mechanism in Scheme I implies that cyclization of citral (**1**) to the more congested biradical **16** becomes more feasible with increasing temperature, and that, through migration of the

Scheme I



formyl group, this species can rearrange to **17** and then close to **2**. A similar formyl migration in **7**, favored only at elevated temperature, would yield **15** and then **3**.[16]

We are unfamiliar with any other photochemical transformations obviously related to these rearrangements leading to **2** and **3**.[18] Such 1,2 migrations of acyl groups in free-radical reactions are rare,[19] and we are not aware of any specific example of the shift of a formyl group. We note that other mechanisms leading to **2** and **3** are possible, including concerted, symmetry allowed $[_\pi 2_s + _\pi 2_s + _\sigma 2_a]$ processes.[20] Present knowledge is too limited to permit a choice among the various possibilities, and current efforts are directed toward clarification of this problem.[21]



18 19

References and Notes

(1) For examples of such studies, see P. Suppan, *Ber. Bunsenges. Phys. Chem.*, **72**, 321 (1968); R. B. Cundall and A. J. R. Voss, *Chem. Commun.*, 902 (1968); H. E. Zimmerman and W. R. Elser, *J. Am. Chem. Soc.*, **91**, 887 (1969); J. E. Baldwin and S. M. Krueger, *ibid.*, **91**, 6444 (1969); F. D. Lewis, R. W. Johnson, and D. R. Kory, *ibid.*, **96**, 6100 (1974); W. C. Agosta and S. Wolff, *ibid.*, **98**, 4182 (1976); J. C. Scaiano, J. Grotewold, and C. M. Previtali, *J. Chem. Soc., Chem. Commun.*, 390 (1972); J. D. Coyle, *J. Chem. Soc., Perkin Trans. 2*, 683 (1972); F. D. Lewis, *Mol. Photochem.*, **4**, 501 (1972); M. V. Encina, A. Nogales, and E. A. Lissi, *J. Photochem.*, **4**, 75 (1975); G. Jones, II, and B. R. Ramachandran, *ibid.*, **5**, 341 (1976).

(2) For examples of transformations that occur only on photolysis at elevated temperature but may be rationalized as thermal reactions of photoproducts observed at lower temperature, see P. J. Kropp and W. F. Erman, *J. Am. Chem. Soc.*, **85**, 2456 (1963); H. N. Subba Rao, N. P. Damodaran, and S. Dev, *Tetrahedron Lett.*, 227 (1967).

(3) R. C. Cookson, J. Hudec, S. A. Knight, and B. R. D. Whitear, *Tetrahedron*, **19**, 1995 (1963).

(4) G. Büchi and H. Wüest, *J. Am. Chem. Soc.*, **87**, 1589 (1965).

(5) Irradiations were carried out under nitrogen at the boiling point of the solvent in a toroidal vessel equipped with reflux condenser and warmed by a heating tape. Solvents used (and boiling points) were toluene (111 °C), mesitylene (165 °C), *p*-cymene (177 °C), and *p-tert*-butyltoluene (190 °C). The light source was a centrally mounted 450-W Hanovia mercury lamp equipped with Pyrex filter. From yield data and temperature dependencies we have obtained approximate relative rate constants and approximate relative activation energies. The data gave linear Arrhenius plots for all products over the temperature range 80–177 °C. Suitable controls indicated that **2–6** are stable under the reaction conditions. Separate, high-conversion, preparative experiments using a uranium glass filter ($\lambda > 3400$ Å) gave similar product distributions at various temperatures.

(6) Aldehyde **6** has been prepared previously by base-catalyzed epimerization of **5**.[4]

(7) R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970).

(8) Data for **2**, **3**, **14**, and **18** follow. Comparable data for **8** and **9** were obtained. All these new compounds gave acceptable elemental analyses for carbon and hydrogen. NMR data are at 60 MHz for ^{1}H and 22.63 MHz for ^{13}C. **2:** IR 3000 (w), 2700 (w), 1730 (s) cm^{-1}; ^{1}H NMR δ 0.86–1.33 with s at 0.98, 1.07, 1.15 (m, 11 H), 1.50–2.26 (m, 4 H), 9.57 (s, 1 H); ^{13}C NMR δ_{Me_4Si} 16.7, 20.8, 23.5, 24.7, 28.7, 31.5, 33.9, 40.0, 56.1. **3:** IR 3000 (w), 2700 (w), 1730 (s) cm^{-1}; ^{1}H NMR δ 0.93–1.30 with s at 1.02, 1.15, 1.22 (m, 11 H), 1.36–2.26 (m, 4 H), 9.38 (s, 1 H); ^{13}C NMR δ_{Me_4Si} 17.0, 17.8, 21.6, 26.3, 29.4, 32.2, 34.8, 37.3, 56.3. **14:** IR 1768 (m), 1738 (s) cm^{-1}; ^{1}H NMR δ 0.90 (s, 3 H), 1.07 (s, 3 H), 1.13–1.27 (m, 2 H), 1.37 (s, 3 H), 2.12 (dd, J = 20, 0.5 Hz, 1 H), 2.63 (ddd, J = 20, 3, 3 Hz, 1 H), 3.67 (s, 3 H). **18:** IR 2720 (w), 1690 (s), 1630 (w), 965 (m) cm^{-1}; ^{1}H NMR δ 1.67 (s, 9 H), 2.25 (m, 4 H), 5.97 (dd, J = 16, 8 Hz, 1 H), 6.70 (m, 1 H), 9.47 (d, J = 8 Hz, 1 H).

(9) Eu(fod)$_3$ is tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octandionato)europium.

(10) Y.-R. Naves and A.-V. Grampoloff, *Helv. Chim. Acta*, **44**, 637 (1961), and references cited therein. We thank Dr. W. I. Taylor, International Flavors and Fragrances, Inc., for a generous gift of 3-carene.

(11) J. P. Schaefer and J. J. Bloomfield, *Org. React.*, **15**, 1 (1967); S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961).

(12) F. J. Marshall and W. N. Cannon, *J. Org. Chem.*, **21**, 245 (1956).

(13) H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, pp 241–245 and references cited therein. As is typical with hindered ketones, a substantial amount of the corresponding hydroxy olefin was also formed in this reduction.

(14) Under the conditions employed, acetophenone absorbed ~80% of the incident light.

(15) For a recent contribution to this complex problem and references to other mechanistic studies, see R. O. Loutfy and P. de Mayo, *J. Am. Chem. Soc.*, **99**, 3559 (1977). These authors found that quantum yields for cycloaddition of enones to olefins may be markedly temperature dependent, with both increases and decreases noted in specific cases.

(16) In an attempt to observe the behavior of **7** independently we have pyrolyzed

4 (sealed ampule at 250 °C). The alternative mode of cleavage of the cyclobutane is followed, however, and the only volatile products are the dienal **18**[8] and α-campholenic aldehyde (**19**).[17]
(17) W. C. Agosta and D. K. Herron, *J. Am. Chem. Soc.*, **90**, 7025 (1968), and references cited therein.
(18) For a recent photochemical reaction interpreted as involving the 1,2 shift of hydrogen in a biradical intermediate, see S. S. Hixson and J. C. Tausta, *J. Org. Chem.*, **42**, 2191 (1977).
(19) For discussion, see J. W. Wilt, in "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, pp 411–412 and 479.
(20) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
(21) This investigation was supported by the National Science Foundation through Grant CHE74-21436 and through a predoctoral fellowship to F.B.

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Simultaneous Fluorination and Functionalization of Hydrocarbon Polymers

Sir:

A thermally and chemically resistant fluorocarbon polymer which supports isolated reactive functional moieties would find much utility as a catalyst support, as a template for biochemical or other synthetic applications, and as membranes and separators for chloro alkali cells and batteries. We report some results in which existing hydrocarbon polymers are simultaneously fluorinated and functionalized using various mixtures of fluorine and oxygen to produce a polytetrafluoroethylene-like backbone with varying degrees of functionalization, 5–60% acid fluoride to monomer groups.

There has for several years in our laboratory been an interest in the reactions of mixtures of oxygen and fluorine. Previously, we have used such mixtures as reagents to oxidize inorganic polymers such as boron nitride.[1] Earlier work by Miller and Dittman showed that mixtures of fluorine and oxygen could, for example, convert tetrachloroethylene to 1,1-dichloro-1-fluoroacetyl chloride.[2] Miller described the process as a "fluorine sensitized oxidation" process. Because our process differs in that it converts hydrocarbon polymers to functional *fluorocarbon* polymers we have for brevity called the process "oxy-fluorination".[3] The process of oxy-fluorination was discovered independently by Manley.[4] This process is not limited to polymers, but has been used successfully to oxy-fluorinate neopentane and 1,4-dioxane[5] and to convert *n*-alkanes to perfluoro acids and diacids.[6]

The results of the oxy-fluorination of polyethylene (low density) and polypropylene under varying conditions are presented in Table I. A typical run (5) is shown in Table II: Initial low concentrations of F_2/O_2 in helium are gradually increased to maximum concentration at zero helium flow. Finally, pure fluorine was admitted to remove residual C–H bonds. Overall pressures and temperatures were ambient room values and no attempt was made to decrease or optimize reaction time. All polymers were studies initially in the form of finely divided (>120 mesh) powder form. In subsequent work 5-mil films were used with very little change in the degrees of functionalization. The density of the low density polyethylene starting material, prepared by the method of Hale,[7] was 0.91.

It can be seen from the F_2:O_2 ratios and the COF content (Figure 1) that the degree of functionalization is directly related to the F_2:O_2 ratio. After the reaction, the acid fluoride groups have strong carbonyl infrared stretches at ~1880 cm^{-1} and, after hydrolysis, an acid carbonyl is a prominent infrared feature. The acid fluoride groups were assayed by careful titration with HCl after the sample had been hydrolyzed, vac-

Table II. Run 5 (Table I)[a]

polyethylene wt, g	He, cm^3/m	F_2, cm^3/m	O_2, cm^3/m	Time, days
2.28	40	2.0	0.1	1
	40	4.0	0.2	1
	40	5.0	0.25	1
	20	1.0	0	5
	5	1.0	0	1
	0	1.0	0	4

[a] Yield 6.93 g, ν_{CO} 1882 cm^{-1}, CFO content 0.53 × 10^{-3} mol/g.

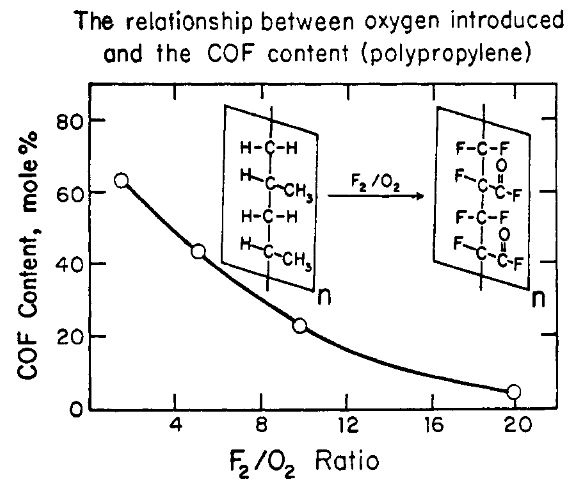

Figure 1.

Table I

Run	Wt, g	F_2:O_2, cm^3/m	Time, days	COF, mol/g	ν_{CO}, cm^{-1}	Anal., % C	Anal., % F	Mp, °C
				Polyethylene				
1	0.52	1.0:1.0	5	4.9 × 10^{-3}	1850			>360
2	10.36	1.0:0.5	17	3.16 × 10^{-3}	1880	26.83	66.78	>360
3	10.84	2.0:0.4	25	1.8 × 10^{-3}	1880	25.62	68.29	>360
4	1.53	2.0:0.2	9	0.78 × 10^{-3}	1880			>360
5	2.28	2.0:0.1	13	0.53 × 10^{-3}	1882			>360
				Polypropylene				
6	1.0	2.0:1.0	9	4.66 × 10^{-3}	1860			110[a] 95[a]
7	5.3	2.0:0.4	35	3.14 × 10^{-3}	1875	25.79	69.23	307[a] 20[a]
8	4.0	2.0:0.2	22	1.53 × 10^{-3}	1880	26.83	68.25	307[a] 305[a]
9	0.6	2.0:0.1	17	0.44 × 10^{-3}	1875			340[a]

[a] Decomposes.

