e.g., it decomposed in large part to an insoluble polymer after 1 hour's standing in the solid state at room temperature.

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A SOLVENT EFFECT IN ALKOXY RADICAL DECOMPOSITION[1]

Sir:

The effect of structure on the competition between alkoxy radical decomposition and attack on hydrogen containing substrates has been the subject of a number of recent papers.[2,3,4] Thus, in the presence of two substrates, three processes are considered to compete, *e.g.*

$$R_1(CH_3)_2O\cdot \xrightarrow{k_1} R_1\cdot + CH_3COCH_3 \qquad (1)$$

$$R_1C(CH_3)_2O\cdot + R_2H \xrightarrow{k_2} R_1C(CH_3)_2OH + R_2\cdot \qquad (2)$$

$$R_1C(CH_3)_2O\cdot + R_3H \xrightarrow{k_3} R_1C(CH_3)_2OH + R_3\cdot \qquad (3)$$

From this scheme, relative reactivities of R_2H and R_3H may be determined, either directly by measuring their relative rates of disappearance when allowed to react competitively, or indirectly by determining ratios of alcohol to ketone produced from the alkoxy radical when reacting with each in turn. Further, if it is assumed that k_2 and k_3 are essentially independent of the structure of R_1 [a quite plausible assumption since bond dissociation energies of alcohols, D(RO-H) appear to be almost independent of structure[5]], relative values of k_1 can be obtained from ratios of ketone to alcohol produced from different alkoxy radicals in the presence of a given substrate.

We have been investigating these competitions during the photo-induced chain decompositions of various *t*-alkyl hypochlorites where reaction (1) is followed by

$$R_1\cdot + R_1C(CH_3)_2OCl \longrightarrow R_1Cl + R_1C(CH_3)_2O\cdot \qquad (4)$$

and (2) and (3) by

$$R_2\cdot \text{ or } (R_3\cdot) + R_1C(CH_3)_2OCl \longrightarrow R_2Cl \text{ (or } R_3Cl) + R_1C(CH_3)_2O\cdot \qquad (5)$$

Techniques have been essentially those described in our previous papers.[6,7] In every case reported the reactions are clearly long chain processes, since reaction mixtures are stable in the dark but react in a few minutes on irradiation with visible light. Further, gas chromatographic analysis shows no significant products other than those predicted by equations 1–5: alcohols, acetone, cyclohexyl chloride, cyclohexenyl chloride and alkyl chloride, R_1Cl. Some typical results are shown in Table I.

TABLE I

DECOMPOSITIONS OF 0.56 M $R_1C(CH_3)_2OCl$ IN $C_2F_3Cl_3$ AT 40° IN PRESENCE OF CYCLOHEXANE (R_2H) AND CYCLOHEXENE (R_3H).

	Product Ratio				
R_1	[R_2H]	[R_3H]	[acetone]/[alcohol]	k_3/k_2[a]	k_3/k_2[b]
CH_3-	1.55	...	~0.05		8.46 ± 0.47[7]
C_2H_5-	1.55	...	1.35		7.54 ± 0.45
	...	1.64	0.325	3.94	
i-C_3H_7-	4.65		16.4		
	...	4.93	13.8	1.12	
t-C_4H_9-	7.75	...	>40		
	...	8.20	>40		
ϕCH_2-	1.55	...	1.28		
	...	1.64	>40	<0.3	

[a] Per molecule, calculated from acetone/alcohol ratio in products. [b] Per molecule, from direct competition.

In the presence of the saturated hydrocarbon substrate (cyclohexane) acetone/alcohol ratios in the products (and presumably k_1) increase with the resonance stabilization of the radical R_1 as anticipated and as has been found by others[2–5] (although the increase for R_1 = benzyl is less than might be expected). In the presence of cyclohexene, acetone/alcohol ratios increase in qualitatively the same manner, but the two sets of data are clearly inconsistent. Further, k_3/k_2 ratios calculated from acetone/alcohol ratios in the presence of cyclohexane and cyclohexene vary markedly for different hypochlorites and, in the one case (R_1 = ethyl) where they can be compared, do not agree with that from direct competition experiments.

The most striking result is provided by the hypochlorite derived from benzyldimethylcarbinol (R_1 = benzyl), and accordingly we have studied it in more detail. Here, in the presence of cyclohexane, substrate attack (giving alcohol and cyclohexyl chloride) and decomposition (giving acetone and benzyl chloride) occur at comparable rates. On the other hand, in the presence of cyclohexene (which should be a more reactive substrate[7]), decomposition is the sole observable reaction; no cyclohexenyl chloride is detected, and only traces of alcohol, probably arising from incomplete conversion to hypochlorite in the original preparation. Conceivably such a result could arise from a drastic change in substrate selectivity (k_3/k_2) with change in alkoxy radical structure. However, *a priori* this seems unlikely and attempts to measure k_3/k_2 by direct competition fail completely since, *in the presence of as little as 5% cyclohexene, chlorination of cyclohexane is entirely suppressed, no consumption of cyclohexene is observed, and alkoxy radical decomposition is the sole detectable reaction.* In short the cyclohexene not only fails itself to react, but apparently induces the decomposition of the alkoxy radical in the presence of an otherwise reactive substrate. Other olefins, including cyclopentene, 1-pentene, 2-hexene, and 4-methyl-2-pentene produce the same result. Negatively substituted olefins such as acrylonitrile and methyl acrylate are slightly less effective, while a variety of aromatic solvents change the acetone/alcohol ratio in the presence of cyclohexane only slightly from that reported in Table I. Further this suppression of substrate attack is not limited to cyclohexane. Small amounts of olefin also

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[1] Partial support of this work by a grant from the National Science Foundation is gratefully acknowledged.

[2] F. D. Greene, M. L. Savitz, H. H. Lau, F. D. Osterholtz and W. N. Smith, *J. Am. Chem. Soc.*, **83**, 2196 (1961).

[3] C. Walling and A. Padwa, *ibid.*, **83**, 2207 (1961).

[4] J. K. Kochi, *ibid.*, **84**, 1193 (1962).

[5] P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959).

[6] C. Walling and B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

[7] C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

completely prevent the chlorination of cyclopentane, 2,3-dimethylbutane, toluene, and ethylbenzene.

These results strongly suggest some sort of interaction or complex formation between the alkoxy radical and olefin,[8] leading to a species which decomposes rather than attacking usually reactive substrates. Why the phenomenon is particularly marked for this alkoxy radical is obscure, but may be related to the relatively large resonance stabilization of the benzyl radical produced in the decomposition.[9] We are investigating these reactions further, but, in the meantime our results indicate not only a striking "solvent effect" in a radical reaction, but also the need for caution in interpreting the results of competitions between reactions 1–3 in studying radical processes.

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[8] Small solvent effects in alkoxy radical reactions have been reported previously, cf. ref. 6, also G. L. Russell, *J. Org. Chem.*, **24**, 300 (1959). However, they have been much smaller than that reported here.

[9] Association of a radical with solvent (since it must involve some stabilization of the system) would be expected to favor those subsequent reactions of the radical having the lowest activation energy. Decomposition of *t*-butoxy radicals has an activation energy several kcal. larger than typical hydrogen abstraction. Here, resonance stabilization of the benzyl radical should greatly reduce (or even reverse) this difference.

[10] University Fellow, 1961–2.

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BOOK REVIEWS

Recent Developments in the Chemistry of Natural Phenolic Compounds. Proceedings of the Plant Phenolics Group Symposium. Edited by W. D. OLLIS, Department of Organic Chemistry, University of Bristol. Pergamon Press, Ltd., Headington Hill Hall, Oxford, England. 1961. viii + 237 pp. 16 × 23.5 cm. Price, $12.00

As the title suggests, this volume is the record of a symposium, in this case the Plant Phenolics Group Symposium held in England in April, 1960. It deserves, however, to be considered as a more basic monograph than this implies, partly since no other basic work covering this field of natural products exists and partly since the contributions here have been expanded with the apparent intent of filling this lacuna. It has only been in recent years, with the rising acceptance of their common biogenetic origin from acetate, that the plant phenolics have been considered as a unit, and the Plant Phenolics Group, which offers this symposium, was organized only five years ago. The present volume should go far toward focusing recognition on this large and important field of natural products, previously dealt with only in isolated fragments, and it is accordingly commendable that this symposium represents many of the foremost authorities in the field.

The book is roughly divided into two parts, dealing with biosynthesis and structure determination, respectively. Of the chapters on biosynthesis, those by Grisebach on isoflavone biosynthesis and Hassall and Scott on oxidative coupling and its laboratory simulation represent excellent, thorough coverages of these fields by their most active practitioners, while the editor has provided an exhaustive and lucid survey, generously larded with formulas, of the origin of isoprenoid units attached to phenolic skeleta. The chapters by Rickards on the work of the Manchester school confirming acetate biosynthesis by tracers and by Whalley on biogenetic relationships deduced from structures are, however, unfortunately both cursory and fragmentary; the material of these two chapters deserves to be considered together, as it is complementary, and to be covered with a thoroughness commensurate with its importance since it has several times previously been treated in this same cavalier fashion.

Of three chapters on the structures of tannin compounds, two (by Haworth and Haslam) are only brief summaries of the corresponding lectures with the explanation that the work is awaiting publication; the reader may well question whether they might not reasonably have been included here in full nonetheless.

The remaining chapters deal with recent structure work which reveals several new families of natural compounds. These areas are covered in detail with clarity, although the chapters (on biflavonyls and the "mycinone" antibiotics) by the editor and his Bristol colleagues occasionally suggest more involvement with establishment of priority than facts. Hörhammer and Wagner have surveyed well the interesting new area of C-glycosides while Dreiding has presented an account of the betacyanins, a complex and still but dimly understood class of plant pigments on which surprisingly little chemical work has apparently been done.

On the whole the book is free of error and the format and formulas are clear and readable. Despite the several cavils above, this volume is a very valuable addition to the book shelf of any natural products chemist.

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Solid State Physics. Advances in Research and Applications. Volume 12. Editors, FREDERICK SEITZ, Department of Physics, University of Illinois, Urbana, Illinois, and DAVID TURNBULL, General Electric Research Laboratory, Schenectady, New York. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. 1961. xv + 459 pp. 16 × 23.5 cm. Price, $16.00.

This is the twelfth volume of a very distinguished series which features key review articles written by top-experts on a wide variety of topics involved in solid state physics. The present issue contains five articles:

I. Group Theory and Crystal Field Theory by C. M. Herzfeld and P. H. Meijer. This article is exceptionally well written. It contains a concise presentation of group theory liberally laced with interesting applications. It will be especially helpful to chemists interested in ligand field theory.

II. Electrical Conductivity of Organic Semiconductors by H. Inokuchi and H. Akamatu. This article summarizes all the information, both theory and experiment, which is not listed as "company secret" on a topic of great interest to both industrial and university chemists. Indeed, there is considerable speculation that semiconductor properties of organic molecules may also play an important role in biochemistry.

III. Hydrothermal Crystal Growth by R. A. Laudise and J. W. Nielsen. The term "hydrothermal" is used to describe reactions taking place at high temperatures and high pressures in the presence of water. Thus, Laudise and Nielsen describe how geophysicists are performing experiments in the laboratory that mother nature carried on in the earth's crust. The unravelling of complicated thermody-