di(p-phenylsulfonylphenyl)propionate, 7705-67-1; p-phenylsulfonylbenzyl iodide, 7718-66-3; p-phenylsulfonylbenzyl methyl ether, 7705-68-2.

Reactions of Aromatic Solids with Halogen Vapors

M. M. LABES AND H. W. BLAKESLEE

*Chemistry Division, The Franklin Institute Research Laboratories,
Philadelphia, Pennsylvania 19103, and the Department of
Chemistry, Drexel Institute of Technology,
Philadelphia, Pennsylvania 19104*

In a recent study of the decomposition of perylene–bromine charge-transfer complex in the solid state, 3,9-dibromoperylene with no trace of monobromo or other dibromo derivatives was formed when the reaction was conducted at temperatures below $-9°$.[1] There are only a few other examples of the use of solid-state forces to control isomer distribution or stereochemistry in an organic reaction. Prelog, *et al.*,[2] observed the spontaneous decomposition of cyclodecyltosylate in the solid state to lead exclusively to *cis*-cyclodecene while the reaction in the liquid phase (acetolysis) yields 20% *cis* and 80% *trans*. Photodimerizations in solids sometimes reflect the geometric consequences of the crystal lattice.[3] Kornblum and Lurie[4] report that when sodium and potassium phenoxides are alkylated heterogeneously, carbon alkylation occurs, whereas the reaction in homogeneous solution gives exclusively oxygen alkylation. They argue that for O alkylation to occur, a linear transition state with a negative charge originally present on oxygen progressively being transferred to halogen is involved; in the solid this is improbable since loss of the charge on oxygen would give rise to strong electrostatic repulsion between the sodium ions which cannot move away from one another in the solid lattice. C alkylation, on the other hand, involves a transition state in which sodium ion nestles between oxygen and halogen atoms, a much more satisfactory geometry.

Bromination of solid anthracene was noted in 1870.[5] The precise conditions were not defined, but presumably the reaction was conducted in the light at room temperature by exposing anthracene powder to bromine vapor. The β form of 9,10-dibromo-1,2,3,4-tetrabromotetrahydroanthracene was said to form. Buckles, *et al.*,[6] studied a large group of aromatic compounds under conditions in which the reaction undoubtedly occurred in a film of solution on the surface of the solid. Our earlier work[1] gave some qualitative observations on the exposure of hydrocarbon films to bromine.

The question which motivated this investigation was to what extent can crystal forces exercise control of isomer distribution in a gas–solid reaction? Accordingly, the chlorination of acetanilide, chlorination and bromination of sodium phenoxide, and photochlorination of benzene in the solid state were examined and the isomer distribution of the products was analyzed.

Many reaction systems were screened in an attempt to find cases where no appreciable vapor pressure of the solid reactant existed or no liquefaction occurred upon condensing reacting quantities of the gas on the solid substrate. The systems studied represent attempts to minimize these possibilities by utilizing primarily high melting point substrates and low reaction temperatures. No macroscopic liquefaction was observed, but a liquid phase existing at the surface can not be rigorously excluded. It was hoped that a charge-transfer complex of some aromatic compounds could be prepared in this way, analogous to the formation of perylene–bromine or condensed aromatic hydrocarbon–iodine complexes. No evidence could be found to indicate that a discrete complex could be prepared *via* a gas–solid interaction for the three compounds studied here in detail; all of the halogen could be removed without reaction occurring by continual pumping at very low temperatures and no visible color changes occurred. The formation of CT complex of benzene–chlorine has been reported;[7] evidently, it is sufficiently unstable to be readily dissociated upon pumping at $-196°$. In all the cases studied, the reaction was conducted at the lowest temperatures at which a reasonable rate prevailed.

The results of the studies of gas–solid halogenations are presented in Table I. The ratios of *ortho* and *para* isomers obtained in this work can be compared with the typical isomer distributions in homogeneous solutions employing molecular halogens and show remarkable agreement. There appears to be little or no effect of crystal forces in these cases on the course of the reaction. Yields are quite high because the surface/volume ratio of the materials is also high.

It was of interest to examine whether the isomer distribution in such a solid–gas reaction varied with per cent reaction. Certainly during the initial portion of the reaction when little or no product has been formed, there is less danger of liquefaction occurring and confusing the results. Table II presents the results of such a study of the chlorination of acetanilide.

Although the results during the short reaction times are not very accurate, there does not appear to be any control of isomer distribution during the early phases of the reaction. The results of Kornblum and Lurie[4] in the heterogeneous reaction of benzyl chloride with potassium *p-t*-octylphenoxide in toluene at 25° were as follows: at 4% completion, there was no O benzylation and exclusively C; at 16% the O–C alkylation ratio was 5:95; and at 100% it was 86:14. This is the only nonphotochemical case we are aware of in which lattice control of product occurs during a surface reaction.

Thus it appears that reactions which occur in the bulk, such as a unimolecular decomposition or the de-

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TABLE I
GAS–SOLID HALOGENATIONS

Compd	Gas	Temp, °C	Time, hr	Total yield, %	Products, %	Usual soln products (%)
Acetanilide	Chlorine	−40	6	50	o-Chloro (30) p-Chloro (70)	o-Chloro[b] (30) p-Chloro (70)
Sodium phenoxide	Chlorine	−80	1.0	79	o-Chloro (24) p-Chloro (28) 2,4-Dichloro (12)	o-Chloro[c] (50) p-Chloro (50)
		−40	0.5	70	o-Chloro (22) p-Chloro (20) 2,4-Dichloro (28)	o-Chloro[c] (50) p-Chloro (50)
Sodium phenoxide	Bromine	0	1.5	65	o-Bromo (5) p-Bromo (60) 2,4-Dibromo (0.2)	o-Bromo[c] (10) p-Bromo (90)
		23	0.5	80	o-Bromo (4) p-Bromo (75) Dibromo (1.3)	o-Bromo[c] (10) p-Bromo (90)
Benzene	Chlorine	−196[a]	4	0.4	α-Hexachlorocyclohexane (47) γ-Hexachlorocyclohexane (7) Δ-Hexachlorocyclohexane (20) ε-Hexachlorocyclohexane (28)	α-Hexachlorocyclohexane[d] (17–41) γ-Hexachlorocyclohexane (32–49)

[a] Illuminated with a mercury vapor lamp.   [b] K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 986 (1927).   [c] Usual yields for halogenation of phenol with molecular halogen in solution; see A. F. Holleman, *Chem. Rev.*, **1**, 187 (1925).   [d] Conditions have been developed in which one may vary the yield of the respective isomers; see R. E. Kirk and D. F. Othmer, "Encyclopedia of Chemical Technology," Vol. 3, Interscience Publishers, Inc., New York, N. Y., 1949, p 810.

TABLE II
ISOMER DISTRIBUTION vs. TIME IN THE CHLORINATION OF SOLID ACETANILIDE AT −40°

Time, min	Isomer distribution of monochloroacetanilide, %	
	ortho	para
5	23	63
15	21	79
3600	30	70

composition of a CT complex, may be expected to show lattice control, whereas those reactions occurring at a surface may not be influenced by the lattice. Studies are planned to examine this aspect of solid-state photoreactions as well as to examine other thermal reactions.

Experimental Section

Chlorination of Acetanilide.—A sample of solid acetanilide was carefully dried at 10^{-6} mm, cooled to −40°, and opened to a chlorine reservoir on the vacuum system which was also held at −40° (vapor pressure of chlorine was 549 mm). After exposure for a given time, the chlorine reservoir was cooled to −196° and the chlorinated acetanilide was removed. Analysis was conducted by converting to chloroanilines by boiling with 20% aqueous hydrochloric acid, neutralizing, extracting, and determining isomer distributions on a Perkin-Elmer Model 154D vapor fractometer fitted with a 15-ft column packed with

"Amine 220" and potassium hydroxide. Extremely good separation of *ortho* and *para* isomers was attained.

Chlorination and Bromination of Sodium Phenoxide.—Sodium phenoxide was prepared as described by Dorofeenko[8] and heated under vacuum to remove traces of phenol until constant weight was achieved. Exposure to halogen was conducted in the same manner as described for acetanilide. After neutralizing and extracting, the mixed mono- and dihalophenols were analyzed chromatographically using a Perkin-Elmer 154D vapor fractometer and a column described by Kolloff.[9]

Photochlorination of Benzene.—A small quantity of benzene was cooled to −196° on a vacuum train and approximately a sixfold excess of chlorine was condensed into this chamber in the dark. The vessel was filled with nitrogen to bring to 1 atm. After holding at −196° for 1 hr, the sample was illuminated with a Hanovia utility mercury vapor lamp held over the dewar flask. The sample is then allowed to warm to room temperature in the dark to remove unreacted benzene and chlorine, leaving the mixed hexachlorocyclohexanes as a crystalline product. Analysis was accomplished by vapor phase chromatography as described by Esselborn and Krebs.[10]

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