Quantitative Study of the Anisotropic Character of a Gas–Molecular Solid Reaction: Chlorine–2-Methylphenol

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Abstract: The anisotropic character of the reaction between solid 2-methylphenol and chlorine gas is described. The amounts of 6-chloro- and 4-chlorophenols obtained vary according to whether the reacting plates of 2-methylphenol have been cut parallel or perpendicular to the *c* axis. This result is obtained whatever the percent conversion. The variation of the ortho:para chlorination ratio according to the crystallographic direction is correlated with the crystal structure of the 2-methylphenol. The results obtained are compared with various mechanisms proposed for this reaction. It is shown that the existence of two reaction paths differentiated before the transition state is in agreement with theoretical chemistry data.

The chemistry of the organic solid state has been studied in depth, for about 15 years by the group of Schmidt and Cohen.[1] More recently papers have been published, especially by Paul and Curtin,[2] dealing with the reactions of organic solids with gases. We have become interested in several aspects of the chemical reactions of single crystals of various phenols with gases.[3] In this article, we will describe the anisotropic character of the reaction of solid 2-methylphenol with chlorine gas. This reaction gives mainly the monochloro products, i.e., the 6-chloro- and 4-chloro-2-methylphenols. The ratio of the reaction products varies according to the crystallographic orientation of the reactant surfaces.

Experimental Section

The single crystals of 2-methylphenol were obtained by the melting bath method from a sample purified by zone melting.[4] They are perfectly transparent and they can attain a large size (volume 1 to 15 cm^3). A typical crystal (shown in Figure 1) is a rod extended along the *c* axis.

A rotation picture along the needle axis gives the "*c*" parameter and the Weissenberg pictures taken about the same axis give the lines of the reciprocal lattice with a reciprocal angle of 60°. Optical goniometric measurements with a Nedensco two-circle goniometer have been made on several crystals mounted with the *c* axis along the rotation axis of the goniometer head. The angles between the normals to the faces have values around 30°, so the crystal is a trigonal prism with $(10\bar{1}0)$ and $(11\bar{2}0)$ faces. The unit cell dimensions are: $a = 16.43$ (3) Å and $c = 5.94$ (2) Å; there are nine molecules in the unit cell.[5] The space group is either $P3_1$ of $P3_2$. The molecules are linked by hydrogen bonds to form three chains parallel to the *c* direction. From these single crystals, we have cut plates of 1 or 2 mm thickness with a surface area of 1.5 cm^2, some parallel to the *c* direction, others perpendicular to the *c* direction. Each plate was placed in a cup that permits collection of the reaction products. In the first series of experiments, two plates were placed simultaneously in the thermoregulated reactor at 0 °C, each one corresponding to a given crystallographic direction. The reactor was evacuated and a known quantity of gaseous chlorine introduced (500 cm^3 at atmospheric pressure). In the second series of experiments, reactions were carried out plate by plate with different amounts of chlorine being introduced into the reactor.

The ratio of the reaction products and the conversion ratio were estimated by vapor phase chromatography. Chromatographic analyses were made with an Intersmat apparatus, IGC 12M Model, equipped with a hot-wire detector. The column was filled with Chromosorb W 60/80 impregnated with diethylene glycol succinate. The peak area was determined with the help of an LTT M 924 numerical integrator coupled with the chromatograph.

Results and Discussion

Two chromatograms obtained under the same conditions are shown in Figure 2; one corresponds to a plate cut perpendicular to the *c* direction, the other to a plate cut parallel to the *c* direction. These plates were chlorinated simultaneously. The ratio[6] of ortho chloro product to para chloro product which we shall call the ortho/para ratio or simply o/p ratio is higher for the plate cut perpendicular to the *c* direction.[7]

The results of all such experiments are plotted in Figure 3. The values corresponding to a 30% conversion ratio, represented by triangles and squares, have been given previously.[8]

We observed that: in all cases, the o/p ratio for a plate cut perpendicular to the *c* axis is higher than the o/p ratio obtained with a plate cut parallel to the *c* axis; the o/p ratio remains similar whatever may be the plane of incision parallel to the *c* direction; for a 2-methylphenol single crystal, we obtain an o/p ratio of 0.51 at 30% conversion ratio; the proportion of 4,6-dichloro-2-methylphenol formed is always small (less than 5%); the results are reproducible if we consider plates of different crystals; likewise, they are reproducible if we chlorinate different plates in independent experiments.

How can we explain the experimental results?

First of all, we realize that there exist irregularities on the faces and one can imagine that different values of the o/p ratios are the result of these irregularities. However, we have to note that the same slicing and polishing procedure was used for all the plates. Furthermore, and this is a more important argument, the selectivity is constant whatever the conversion ratio but different according to the direction. It is unlikely that the same irregularities are present on a face after many layers of molecules have been removed by the reaction as were present at the beginning of the reaction. These irregularities could explain changes in the o/p ratio for a small conversion ratio but not for a high conversion ratio of say 30%. Finally, the attack by chlorine gas of a single crystal appears to be a method of obtaining a smooth surface,[9] so the attack has to change the pattern of irregularities.

The experimental results can be understood if we consider the orientation of the 2-methylphenol molecules within the crystal and the accessibility of the reactive sites, accessibility which is related to the orientation factor.[10] For isolated 2-methylphenol molecules there exists a given o/p ratio which is the same for all the molecules but can be different from one;[11] in the solid state this ratio is affected by the accessibility to the reactive sites.

With a plate cut perpendicular to the *c* axis the accessibility to the ortho or para positions is the same if the attack is allowed on the two opposite faces of the plates.[12] For plates cut parallel to the *c* axis, ⅔ of the molecules have the same orientation as for a plate cut perpendicular to *c* but ⅓ of the molecules expose, on one face, the nonreactive groups OH or CH_3 and, on the other face, the para position. For instance, if we consider the chlorine attack on faces $(11\bar{2}0)$ the marked molecules (*) on

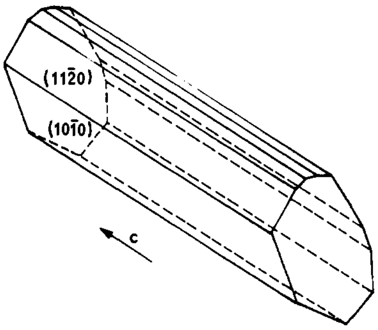

Figure 1. A typical crystal of 2-methylphenol.

the stereoscopic projection on Figure 4 expose either para positions or OH or CH_3 groups. If these molecules expose a para position the reaction should mainly produce the 4-chloro-2-methylphenol. If an OH or a CH_3 group is exposed the reaction should not occur as long as the molecule is within the lattice but should occur afterwards in the polar disordered reaction medium for which the o/p ratio is close to 0.4.[11] All the arguments we developed for (11$\bar{2}$0) faces are valid for faces like (0110) or (1010). The particular orientation of ⅓ of the molecules could explain why the o/p ratio is smaller for faces cut parallel to the *c* axis than for faces perpendicular to that axis.[13] Whatever the plate the conversion ratio is the same[14] when two plates, one cut perpendicular to the *c* axis and the other parallel to *c*, are simultaneously chlorinated; thus, the selectivity change cannot be explained by a modification of the total reaction rate with respect to the reaction front direction.

A 2-methylphenol single crystal which reacted completely with chlorine gave an o/p ratio similar to the one obtained for plates cut parallel to the *c* direction. This result can be explained on the basis that the faces parallel to the *c* axis have a surface very much greater than those of the faces perpendicular to the *c* axis.

An alternative explanation is to consider a much more subtle differential effect of the solid matrix in the stabilization of the transition states of the two competing reactions. In the transition states of the molecules within the crystal it is possible that charges can be delocalized differently for the ortho and para positions when the chlorine molecule's approach is either parallel to the *c* axis or perpendicular to it. The situation is too complicated to permit further development of this explanation.

The above explanations do not take into account the possibility of chlorine molecules diffusing inside the bulk crystal; in fact, this is improbable since the minimum dimension of a chlorine molecule evaluated by van der Waals contact radii is about 3.6 Å[15] and the largest available channels are about 3.1 Å.

The electrophilic aromatic substitution reaction[16] which we have studied is carried out in the absence of solvent and catalyst. This reaction is a molecular one whose mechanism has not been thoroughly studied. However, according to Olah's conclusions,[17] the limiting step of the chlorination reaction corresponds either to a unique transition state (of the π complex type) which leads to substitution in the ortho and para positions or to two different transition states, one of them producing an ortho-substituted compound and the other a para-substituted compound. In a schematic analysis one can conclude that in the first case the o/p ratio is fixed while in the second case this ratio can change according to the experimental conditions. The anisotropy of this gas-organic solid reaction suggests that the chlorination of 2-methylphenol is a reaction proceeding through two reaction paths, each of which has one transition state, one corresponding to ortho substitution and the other to para substitution.[18] It is worthwhile then to check if the two-transition-state explanation is consistent with theoretical chemistry calculations.

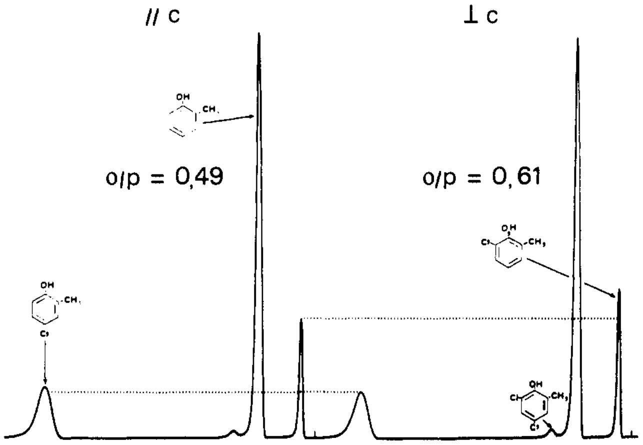

Figure 2. Two chromatograms obtained under the same conditions: one corresponds to a plate cut perpendicular to the *c* direction, the other to a plate cut parallel to the *c* direction.

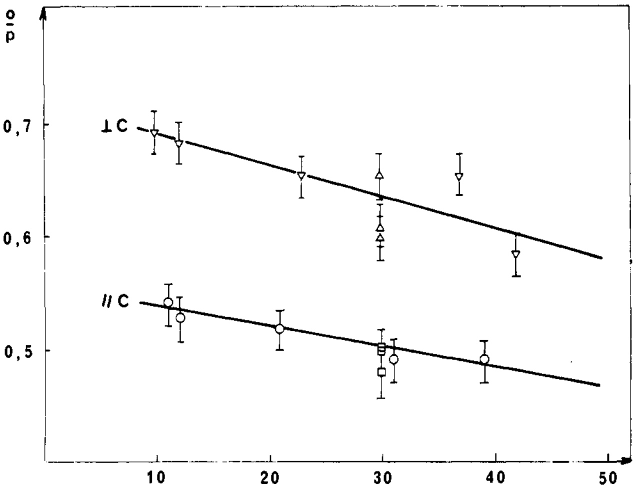

Figure 3. o/p ratio plotted against conversion ratio. Error bars indicate analytical errors.

For the theoretical calculations, we have selected the direction of approach of the chlorine molecule perpendicular to the plane of the aromatic nucleus. The Cl–Cl bond is parallel to this direction. This choice was suggested by the works of Hassel and Stromme.[19] These authors showed by crystallographic studies of a 1:1 chlorine-benzene complex that the chlorine molecule is perpendicular to the plane of the aromatic nucleus. In this direction, we have specified the energetically more favored modes of approach of the chlorine molecule to the 2-methylphenol molecule and the most probable reaction intermediates. This study was carried out using the CNDO II method with the parameters first proposed by Pople.[20] We have looked at the vertical approaches to the center of the aromatic nucleus, to the carbon atom at the ortho position, and to the carbon atom at the para position. The calculation of the energy difference between the complex and the two isolated molecules shows that a stable complex exists when the distance from a particular chlorine atom to the nearest aromatic ring is 4 Å. This complex may have a geometry similar to that of the complex isolated by Hassel and Stromme.[19] These authors obtained a distance of 3.28 Å for the distance between a particular chlorine atom and the nearest aromatic ring.

Figure 5 gives the energy difference between the chlorine–2-methylphenol supersystem and the isolated molecules vs. the distance between the two reactants. These curves show that

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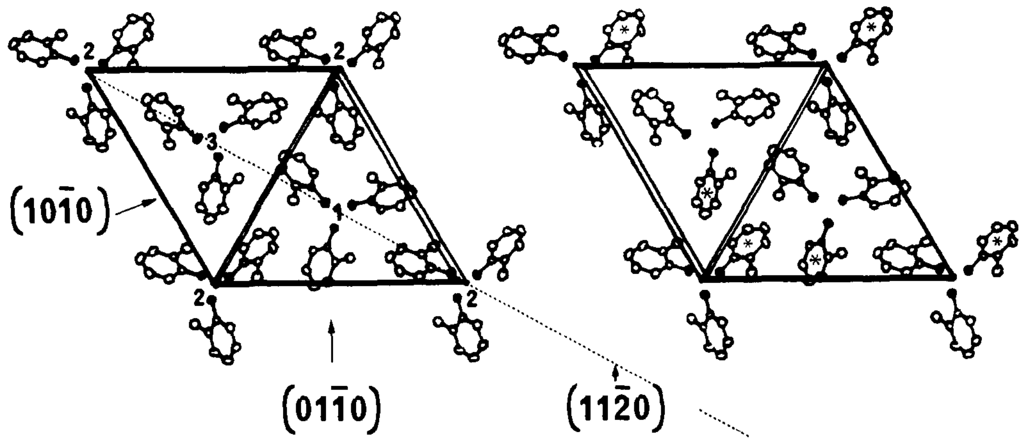

Figure 4. Stereoscopic view of the crystal structure of 2-methylphenol: (○) carbon; (●) oxygen; hydrogen atoms have been omitted. The marked molecules expose on faces (11$\bar{2}$0) either para positions or OH or CH_3 groups.

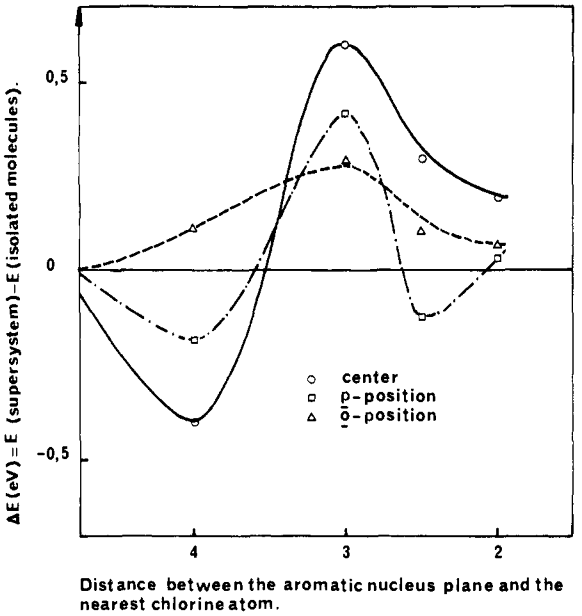

Figure 5. Energy difference between chlorine-2-methylphenol supersystem and the isolated molecules vs. the distance between the aromatic nucleus plane and the nearest chlorine atom.

the energy barriers are a maximum at 3 Å and the values are as follows: center of ring, 0.600 eV (13.83 kcal/mol); para position, 0.424 eV (9.77 kcal/mol); ortho position, 0.296 eV (6.82 kcal/mol).

Thus, two potential barriers are exhibited, one for ortho substitution and the other for para substitution. These two approaches are more favored than the one vertical to the center of the aromatic nucleus. This agrees with our experimental results, for if the approach to the center of the aromatic nucleus were the more favored only one transition state would govern the reaction and the o/p ratio should be constant.

In conclusion, the anisotropy of the reaction between chlorine gas and crystalline 2-methylphenol can be interpreted on the basis of the 2-methylphenol crystallographic data. The anisotropic behavior of the molecular chlorination of phenols leads us to choose a mechanism with two reaction paths, the branching occurring before the transition states. This conclusion is in agreement with results from theoretical chemistry.

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References and Notes

(1) (a) M. D. Cohen and G. M. J. Schmidt, "Reactivity of Solids", J. H. De Boer, Ed., Elsevier, Amsterdam, 1961, p 556 ; (b) M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.*, 1996 (1964), and following papers; (c) G. M. J. Schmidt, *Pure Appl. Chem.*, **27**, 647 (1971); (d) M. D. Cohen and B. S. Green, *Chem. Br.*, **9**, 490 (1973).

(2) (a) R. S. Miller, D. Y. Curtin, and I. C. Paul, *J. Am. Chem. Soc.*, **93**, 2784 (1971); (b) C. T. Lin, I. C. Paul, and D. Y. Curtin, *ibid.*, **96**, 6199 (1974); (c) R. S. Miller, D. Y. Curtin, and I. C. Paul, *ibid.*, **96**, 6329, 6334, 6340 (1974); (d) I. C. Paul and D. Y. Curtin, *Science*, **187**, 19 (1975).

(3) (a) M. Perrin, P. Michel, R. Lamartine, and R. Perrin, First European Crystallographic meeting, Bordeaux, 1973; (b) R. Lamartine and R. Perrin, *J. Org. Chem.*, **39**, 1744 (1974); (c) R. Lamartine and R. Perrin, *C. R. Hebd. Seances Acad. Sci.*, **279**, 367 (1974); (d) R. Lamartine, R. Perrin, G. Bertholon, and M. F. Vincent-Falquet, Fourth International Symposium on the Organic Solid State, Bordeaux, 1975.

(4) R. Perrin and M.-F. Berny, "Journées Hellènes de Séparation Immédiate et de chromatographie," Athènes, 1965.

(5) C. Bois, *Acta Crystallogr., Sect. B*, **28**, 25 (1972).

(6) o/p is the ratio of the number of 6-chloro-2-methylphenol molecules to the number of 4-chloro-2-methylphenol molecules.

(7) It is to be noted that the true o/p ratios are different from the experimental ones for the plates have a thickness of 1 to 2 mm. However, the area of the top surface is much greater than the area of the perimeter surface. Thus, for a plate cut perpendicular to the *c* axis the ratio of the areas will be in the 3.5/1 to 7/1 range; for a plate cut perpendicular to the *c* axis the ratio will be in the 7/1 to 14/1 range. In any event if we could obtain the true ratios for very thin plates the change in the ratio will be greater than the one observed.

(8) R. Lamartine, *C. R. Hebd. Seances Acad. Sci.*, **279**, 429 (1974).

(9) R. Perrin, G. Bertholon, R. Lamartine, M. F. Vincent-Falquet, P. Michel, M. Perrin, A. Thozet, and C. Bavoux, *Mol. Cryst. Liq. Cryst.*, **33**, 171 (1976).

(10) T. W. G. Solomons, "Organic Chemistry", Wiley, New York, London, Sydney, Toronto, 1976, p 132.

(11) Very high values were obtained in experimental studies made at low concentrations in a nonpolar solvent (M.-F. Vincent-Falquet and R. Lamartine, *Bull. Soc. Chim. Fr.*, 47 (1975)). In a polar solvent the ratio was close to 0.4.

(12) As we said before we were not able to attack selectively one or the other of the two faces of a plate. We do not know at the present time how to protect a given face from the chlorine reaction.

(13) With the explanations we proposed it is possible to determine the o/p ratio for a plate cut parallel to the *c* axis if the o/p ratio of plate cut perpendicular is known. For instance with a conversion ratio of 30% the o/p ratio of a plate cut perpendicular to *c* is 0.62. For a plate cut parallel to *c*, ⅔ of these molecules give an o/p ratio of 0.62, for the other third, half of them gives an o/p ratio of 0.4 and the other half reacts mainly on the para position. The theoretical ratio is then 0.48, a value in very good agreement with the experimental figure of 0.50.

(14) See the results for the 30% conversion rate.

(15) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 260.

(16) P. B. D. de la Mare and B. E. Swedlund, "The Chemistry of the Carbon Halogen Bond", S. Patai, Ed., Wiley, Chichester, England, 1973, p 500.

(17) G. A. Olah, "Friedel-Crafts Chemistry", Wiley, New York, London, Sydney, Toronto, 1973, pp 476–542.

(18) M. Lahav, Seminar, Lyon, 1974.

(19) O. Hassel and K. O. Strömme, *Acta Chem. Scand.*, **5**, 1146 (1958); **9**, 1781 (1959); O. Hassel and C. Romming, *Q. Rev. Chem. Soc.*, 1 (1962).

(20) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, 3129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **43**, 3136 (1965); **44**, 3289 (1966).