

Carbon Tetrachloride: A New Crystalline Modification

Abstract. *X-ray and optical studies of single crystals of carbon tetrachloride have established the existence of a previously unreported rhombohedral modification stable between the melting point and the transition temperature. The discovery of this phase emphasizes the need for a careful reinterpretation of available measurements of the thermal properties of solid carbon tetrachloride.*

As part of a systematic low-temperature x-ray diffraction study of the solid-solid phase transitions occurring in the methylchloromethane compounds $[(CH_3)_nCCl_{4-n}]$, where n varies from 0 to 4], we have investigated the temperature ranges of stability of the solid phases of carbon tetrachloride. A previously unreported rhombohedral modification, which appears to be stable in the same temperature region as the known face-centered cubic phase (1), has been detected; of the two, the rhombohedral phase is the more stable. We have also found that below -47.7°C an ordered, monoclinic form of carbon tetrachloride is stable and is isostructural with corresponding modifications of carbon tetrabromide and carbon tetraiodide (2).

Carbon tetrachloride freezes at -22.75°C (3) and undergoes a crystallographic phase transition at -47.7°C (4). Optically isotropic crystals are formed by careful freezing of liquid carbon tetrachloride; these have been previously described and are face-centered cubic (1). When these crystals are maintained in the temperature region in which they have been reported to be stable, they transform spontaneously to a rhombohedral modification after several hours. When crystals of either high-temperature modification are cooled below -47.7°C , a monoclinic phase is formed. Warming the monoclinic crystals above -47.7°C induces a transition to the rhombohedral phase. In no case was the face-centered cubic phase detected when the monoclinic phase was heated above the transition temperature.

Identification of the rhombohedral phase between crossed polaroids was difficult. Single crystals of all three crystalline forms of carbon tetrachloride shatter when they undergo solid-phase transformations. Although the monoclinic phase is strongly birefringent and is easily identified, the polycrystalline form of the rhombohedral phase is weakly birefringent and, when it is enclosed in the thin-walled glass capillary tubes used to hold the sample, it could readily be mistaken for the polycrystalline isotropic phase. In fact, the

existence of a rhombohedral phase was not even suspected, in spite of repeated optical examination between crossed polaroids, until the x-ray photographs established its presence.

Single crystals of all three modifications were grown from samples sealed in thin-walled glass capillary tubes (0.2 mm diameter) mounted on x-ray cameras adapted for low-temperature studies (5). Oscillation, rotation, and Weissenberg photographs were obtained with $\text{CuK}\alpha$ radiation; crossed polaroids were used to aid in detecting and orienting birefringent phases. Identical results were obtained with samples of carbon tetrachloride from several sources, varying from highly purified specimens, shown by vapor phase chromatography to have a purity greater than 99.9 percent, to ordinary commercial samples. The size and shape of the specimen container also had no detectable effect.

The rhombohedral and monoclinic modifications appear to be simply related to the face-centered cubic form. The edge of the unit cells of the rhombohedral form is equivalent in length to $\sqrt{3}$ times the cubic unit cell edge (that is, to the length of the body diagonal). It is, however, difficult on this basis to account for the observed rhomboidal angle (α) of 90° . The body diagonals of a cube meet at angles of $70^\circ32'$. The shat-

tering of single crystals of the face-centered-cubic phase as they spontaneously transform to the rhombohedral modification appears to result from the major molecular rearrangements needed to convert the $70^\circ32'$ angles of the cubic phase to the 90° angles of the rhombohedral form.

It can also be shown that the monoclinic unit cell is built up from slightly distorted cells closely related to the cubes of the face-centered cubic phase ($d_{101} \cong 2a_{\text{cubic}}$; $d_{010} \cong d_{10\bar{1}} = \sqrt{2}a_{\text{cubic}}$; and the angle between $[101]$ and $[10\bar{1}]$ is 91.4°). The monoclinic axes given in Fig. 1 were chosen to be consistent with those reported for the isomorphous, low-temperature forms of carbon tetrabromide and carbon tetraiodide (2).

Our results, obtained at 1 atm from -25° to -150°C , are consistent with those reported by Bridgman (6); he detected three solid forms of carbon tetrachloride stable below 100°C and at pressures up to 10,000 atm.

Although the transition temperature of carbon tetrachloride has been proposed as a fixed point for low-temperature thermometry, a number of workers have reported discrepancies in the measured transition temperatures. The discrepancies were sufficiently large and persistent to prompt Hicks, Hooley, and Stephenson (4) to observe that "... the differences observed between the temperature obtained when the equilibrium is approached from the low-temperature phase and the temperature obtained by cooling from the high-temperature phase indicate that equilibrium cannot be reached in a reasonable period of time. . . ." Our findings indicate that warming monoclinic carbon tetrachloride to the

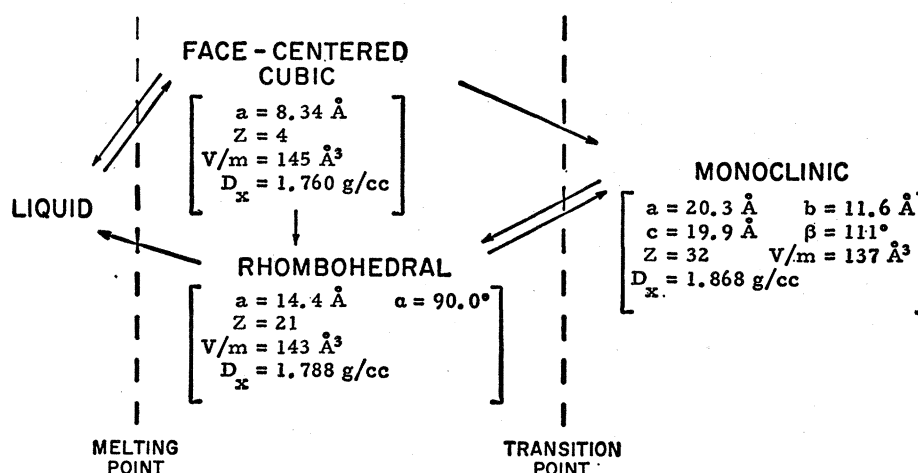


Fig. 1. Carbon tetrachloride: crystal data and direction of phase transitions (Z , molecules per unit cell; V/m , volume/molecule; D_x , x-ray density).

rhombohedral form involves different processes from those involved in cooling face-centered-cubic carbon tetrachloride to the monoclinic form. A redetermination of the heat capacity and of related thermodynamic quantities of carbon tetrachloride, taking into account the results of our work, appears necessary.

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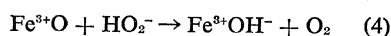
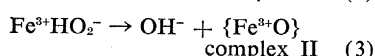
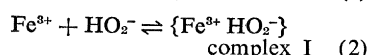
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Photochemical Evolution of Oxygen from Certain Aqueous Solutions

Abstract. *Illumination of aqueous solutions containing ferric ions and hydrogen peroxide leads to evolution of O₂ by way of a chain reaction. The photochemically active intermediate is the complex between Fe³⁺ and HO₂⁻. The effects of pH and concentration of the reagent on the quantum yield (chain length) are reported.*

The catalytic decomposition of H₂O₂ by Fe³⁺ ions in a thermally activated dark reaction was shown (by parallel kinetic and spectrophotometric measurements in acid solutions of hydrogen peroxide and ferric perchlorate) to proceed by the following mechanism (1-3):



This involves complex formation between ferric ion and the anion of hydrogen peroxide (4-6). Electron transfer does not take place within this complex, as had been assumed (7). The first complex must be transformed (1), in the slow rate-determining step (re-

action 2), into complex II, in which O is covalently bound to iron; in this step OH⁻ ions are displaced into the solution (3). Steps 1 to 3 thus result in elimination of a molecule of water from the reactants. Complex II may then react with a second HO₂⁻ to produce evolution of O₂ by hydride transfer. Elucidation of the reaction mechanism required work with solutions containing ~10⁻³M Fe³⁺ and 10⁻²M (or less) H₂O₂.

Details of the reaction mechanism, the relation to cocatalysis by copper, and the extension of these concepts to the decomposition of hydrogen peroxide by haemin were elaborated by Kremer (3, 8); the mechanism is closely related to that resulting from the work of Jones, Wynne-Jones, and co-workers with more-concentrated peroxide solutions—higher than 1M (9). Jones and Wynne-Jones (10) also support the view that such a mechanism may be applicable to the catalase-induced decomposition of hydrogen peroxide.

Light of greater wavelength than 300 nm is not significantly absorbed by either Fe³⁺ or H₂O₂ alone in solutions comparable to those employed by the workers mentioned; mixtures of these components do absorb at greater wavelength because of the formation of the intermediate complexes. Absorption by the Fe³⁺OH⁻ complex (6) also must be considered. Complexes I and II have different absorption spectra, that of complex I extending further into the visible and near-ultraviolet (1). As the reaction mechanism indicates, absorption due to complex II can be observed only at low concentrations of peroxide; at higher concentrations of H₂O₂, the dominant absorption is due to complex I. Complex I was observed by Evans, George, and Uri (4), who assigned the band, with λ_{max} = 350 nm, to an ion-pair complex between Fe³⁺ and HO₂⁻. This assignment is supported, and the light-absorption process is interpreted (2) as electron transfer from HO₂⁻ to Fe³⁺ (in the inner hydration sphere which it has entered), by correlation with energetic data. These data show (2) that HO₂⁻ itself, in aqueous solution, possesses a charge-transfer-to-solvent absorption band (11). In the presence of Fe³⁺ the new absorption band observed fits the energetic correlation that holds (12) for the anion-to-Fe³⁺ electron transfer of other anions having charge-transfer-to-solvent bands.

If the reaction mechanism proposed

Table 1. Derivation of the rate constant of the light-induced reaction, from results of mixed decompositions (thermal and photo) at various temperatures; [Fe³⁺], 5.36 × 10⁻³M; [H₂O₂]_{initial}, 0.24M; pH, 2.10.

<i>T</i> (°C)	Combined reactions— thermal and photo (10 ³ × <i>k</i> _(<i>t</i>+<i>p</i>) , min ⁻¹)	Photoreaction alone, calc. (10 ³ × <i>k</i> _{<i>p</i>} , min ⁻¹)
14.0	16.4	2.4
10.0	13.1	3.8
5.0	7.4	3.4

for the catalytic dark reaction holds, so that electron transfer does not occur within complex I, and O₂ evolution must await the slow rearrangement to complex II, it may be possible to cause photochemical evolution of oxygen from such solutions, under conditions in which the thermal reaction is slow, by light-induced electron transfer from HO₂⁻ to Fe³⁺ in the absorption band of complex I. In this case, free-radical formation, which does not take place in the dark catalytic mechanism proposed, may indeed occur.

This determination required experiments to be carried out in solutions at H₂O₂ concentrations that assured sufficient absorption of light at wavelengths greater than 300 nm, but which were low enough to enable one to determine reliably the difference in H₂O₂ concentration in the course of the reaction. This requirement necessitated the use of solution in the range between the low concentrations employed by Kremer and Stein and the high concentrations used by Jones and Wynne-Jones. Such experiments were performed (13) in the temperature range 5° to 27°C at H₂O₂ concentrations between 0.01 and 1M. Rate constants obtained, in good agreement with the results in the lower and higher ranges, showed the general applicability of the catalytic mechanism.

In our photochemical experiments, high-purity ferric perchlorate, perchloric acid, and hydrogen peroxide were used with specially purified water in a

Table 2. Quantum yield at ~ 365 nm; *T*, 5.5°C; [Fe³⁺], 5.36 × 10⁻³M.

[H ₂ O ₂] ₀ (M)	pH	Quantum yield (φ)
<i>Dependence on initial [H₂O₂]</i>		
0.556	2.06	7.42
.290	2.06	5.17
.160	2.06	3.31
<i>Dependence on pH</i>		
0.290	2.06	5.17
.279	1.50	6.22
.274	1.22	7.78