with the intensity when this is changed several fold; this is taken to indicate a first-power dependence of the rate on intensity. In experiments 15 and 17 the intensity was changed about fourfold within each run.

In dilute carbon tetrachloride solution, the quantum yields of this reaction likewise showed little dependence on concentrations or intensity; but the yields were less than one one-hundredth as great as in the gas phase. The high yields in the gas phase leave no doubt as to the chain character of the reaction.

Concerning a possible mechanism of the oxidation, two remarks may be made. First, in view of the different dependence of rate on intensity in the oxidation and chlorination, the chain breaking step presumably differs in the two cases. Second, the fact that when the oxygen concentration has fallen to a low value the total rate of reaction is less than either that of the preceding oxidation or that of the subsequent chlorination suggests that oxygen enters in two different ways—a chain oxidation and a chain-breaking oxidation. For example, with sufficient oxygen present, Cl might usually form ClO_2 and this lead to chain oxidation; with little oxygen, Cl might usually form C_2Cl_5 and this be oxidized without the continuance of a chain.

Summary

A chlorine-sensitized photo-oxidation of tetrachloroethylene in the gaseous state has been carried out with radiation of the wave length 4358 Å. The products have been found to be largely trichloroacetyl chloride with some phosgene. Quantum yields of about 300 molecules of tetrachloroethylene oxidized per quantum absorbed have been obtained; no strong dependence of the yields on concentrations or light intensity has been found.

Chlorination to hexachloroethane in the absence of oxygen also has been found to go as a chain reaction with rates fairly well represented by the equation $-d(Cl_2)/dt = k(I_{abs.})^{1/2}(Cl_2)$. Possible mechanisms have been discussed.

Pasadena, California Received March 26, 1934

[Contribution from Westinghouse Research Laboratories]

The Dielectric Properties of Cellulose

By W. N. Stoops

Cellophane has a number of properties which suggest that it would be superior to paper as a dielectric. It is not highly porous and has both a higher dielectric constant and a higher dielectric strength than paper. On account of these desirable properties, it was decided to undertake a rather thorough investigation of its electrical properties, particularly the dielectric constant and power factor, considering their variation with temperature, frequency and the presence of various materials with which cellophane may be impregnated. For example, it readily absorbs moisture from the air, and this adsorbed water profoundly affects its electrical properties. It is hoped to discuss this effect in a later paper, but here only dried glycerol-free cellophane will be considered.

Experimental

A modified Schering bridge was used for dielectric constant and power factor measurements at frequencies below 100,000 cycles and a resonance circuit at higher frequencies. The bridge is similar to the one reported on by Dr. A. V. Astin before the Baltimore meeting of the Committee on Insulation of the National Research Council in November, 1932. As in his bridge, the source and detector were interchanged with the result that the detector could be at ground potential, thus simplifying the shielding and permitting the use of a Wagner earthing device. However, it was found that this Wagner ground was not necessary except for measuring very small power factors—less than 0.01—and so the bridge was grounded directly without its use. The bridge was balanced entirely by variation in capacitance, General Radio precision condensers type 222 being used throughout. A two-stage capacity-resistance coupled amplifier was used on the output of the bridge and gave satisfactory amplification over the entire frequency range. A vibration galvanometer was used as detector at frequencies below 1000 cycles, headphones at 1000–3000, and a heterodyne method at higher frequencies. A General Radio variable frequency oscillator was used as a power source at all frequencies below 100,000 cycles. A resonance circuit recommended by the American Society for Testing Materials[1] was used for the capacity and power factor measurements at higher frequencies. It was modified by

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[1] Proc. A. S. T. M., Vol. 31, I, p. 877, and 1931, T. S., p. 642.

introducing an intermediate tuning circuit between the oscillator and the measuring circuit to remove any harmonics in the wave form and to make it possible to maintain the sample under constant voltage.

A large Dewar tube filled with toluene served as a constant temperature bath. The low temperatures were obtained by the use of liquid air[2] and those above room temperature by means of a small heating coil. A platinum resistance thermometer was used to measure temperature.

The sample of cellophane to be studied was mounted in an all-glass U-shaped cell, so that mercury could be poured in from either side to form the electrodes. The samples were dried in the cell by heating at 105° until further heating left the electrical properties unchanged.

Results

The data for cellophane are presented graphically in Figs. 1 to 4. Figures 1 and 2 show the variation of dielectric constant and power factor, respectively, with temperature at the different frequencies used. Satisfactory measurements could not be made at temperatures below the freezing point of mercury, as it was impossible to obtain good contact with solid electrodes.

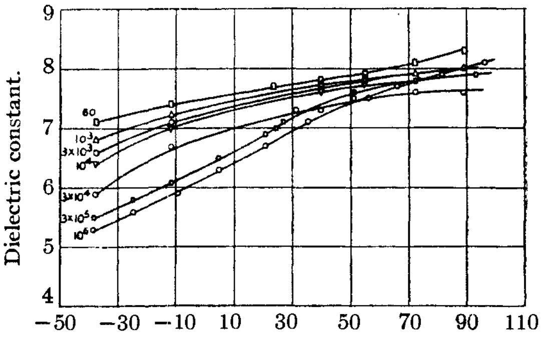

Fig. 1.—Dielectric constant *vs.* temperature at different frequencies for dried g. f. cellophane.

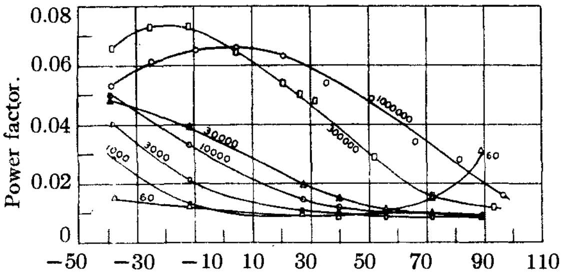

Fig. 2.—Power factor *vs.* temperature at different frequencies for dried g. f. cellophane.

The variation of dielectric constant and power factor with frequency at three different temperatures is shown in Figs. 3 and 4. Table I gives values of dielectric constant and power factor at 22° of regenerated cellulose or cellophane, and of cellulose acetate film. The cellulose acetate was a practically pure specimen of triacetate prepared by Professor Berl of Carnegie Institute of Technology.

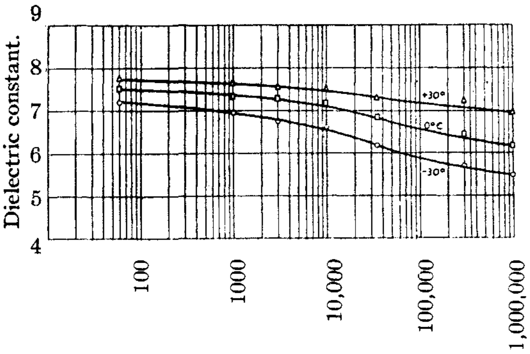

Fig. 3.—Dielectric constant *vs.* frequency for dried g. f. cellophane.

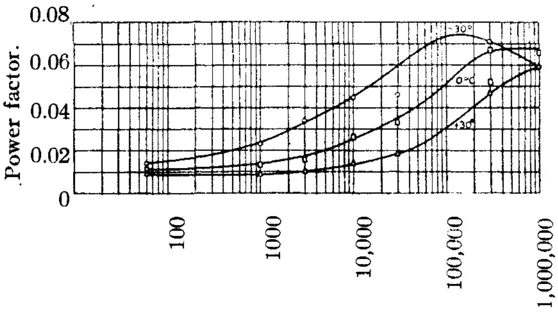

Fig. 4.—Power factor *vs.* frequency for g. f. dried cellophane.

Discussion

The dielectric constant data, as shown in Figs. 1 and 3, have a rather uniform variation with temperature and frequency. Although the dielectric constant increases with temperature at all frequencies, this increase becomes progressively less as the frequency drops from 1,000,000 to 60 cycles. The power factor values, however, increase with decreasing temperature, those at the two highest frequencies going through a maximum. This is the sort of dependence on temperature and frequency that has been found for polar liquids[3] of both low and high viscosity. This same behavior has been discovered in at least one solid, ice.[4] Most polar liquids on freezing under-

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[2] Walters and Loomis, THIS JOURNAL, **47**, 2302 (1925).

[3] See Mizushima, *Institute of Physical and Chem. Research (Tokyo)* **5**, 201 (1927); and White and Morgan, *J. Franklin Inst.*, **216**, 635 (1933).

[4] Debye, "Polar Molecules," The Chemical Catalog Co., Inc., New York, p. 102.

TABLE I

Freq.	60 cycles		1000		10,000		300,000		1,000,000	
	d. c.	p. f.	d. c.	p. f.	d. c.	p. f.	d. c.	p. f.	d. c.	p. f.
Cellophane	7.7	0.009	7.6	0.010	7.3	0.016	7.0	0.053	6.7	0.062
Cellulose acetate	4.1	.014	4.0	.018	3.9	.019	3.7	.021	3.7	.019

go a sharp change in dielectric constant and do not show anomalous dispersion in the solid state.[5] Cellophane, however, shows many similarities to the behavior found in ice. We find an increase of dielectric constant with temperature at all frequencies, together with a convergence to a value largely independent of frequency above 70°. The 60-cycle value is slightly higher at this temperature, doubtless due to a conductance polarization. It may be noted that the 60-cycle power factor shows a sharp increase above 70° as a result of an increase in direct current conductance of cellophane above this temperature. Because of possible decomposition, measurements were not made above 100°. The power factor data, Figs. 2 and 4, also show the behavior we would expect in such a polar solid. Anomalous absorption, as shown by a maximum or an increase in the power factor, is greatest at the frequencies and temperatures where the most dispersion, or decrease in dielectric constant, occurs.

However, when we turn to a consideration of the chemical constitution of cellulose in search of a source of this orientation polarization, we find no obvious solution. The empirical formula is $(C_6H_{10}O_5)n$, where n is probably less than 200. Each glucose residue, as the $C_6H_{10}O_5$ unit is called, contains three hydroxyl groups, and the chemistry of cellulose is largely concerned with their reactions. In the sample of cellulose acetate for which data are given in Table I, these three hydroxyl groups have been replaced with acetate radicals so that the material is practically pure cellulose triacetate. This change in composition lowers the dielectric constant of cellulose (cellophane is pure cellulose) nearly 50%, and we also find considerably less anomalous absorption and dispersion. In general, the alcohols have higher dielectric constants than the esters, and we may assume that the smaller dielectric constant of cellulose acetate is due to the substitution of the acetate group for the hydroxyl of the cellophane.

However, it does not seem reasonable to assume that the dispersion and absorption that we find in cellophane at the higher frequencies is due to inability of its hydroxyl groups to respond to the applied field. Their resonant frequency in the molecule should be in the Raman spectral region. Then, too, the data in Table I indicate the same dispersion to exist in cellulose acetate, although less markedly.

Looking again to the literature on the structure of cellulose we find that the belief is rather widely held that the cellulose molecule is a long chain[6] containing 30–40 glucose units, possibly formed as a spiral. Sheppard, Nietz and Keenan[7] have suggested that these chains are grouped together in bunches of 40–60 to form the micelle, being held in a bundle by the fields of force surrounding the polar groups in the chain. These groups occur periodically along the chain and two chains are pictured as being held together as follows $\overset{+}{\circ}\underset{+}{\circ}\overset{+}{\circ}\underset{+}{\circ}\overset{+}{\circ}\underset{+}{\circ}$. Here the plus signs may be considered as indicating a highly polar part of the molecule and the circles a less polar part. The assumption that these units in the chain have a tendency to rotate with an applied field does not seem impossible. They are believed to be held together by an oxygen bond, —O—, and might be free to rotate about it were it not for the restraining forces exerted by neighboring parallel chains. As the temperature is raised, these forces will become less effective and more molecules will be free to respond to an applied field, thus giving an increase in dielectric constant with temperature. An attempt to calculate the size of the rotating molecule or group of molecules from the relaxation time is obviously without meaning in a solid. However, it seems reasonable to expect units the size of those making up the chain in cellulose to show absorption and dispersion in the temperature and frequency range studied.

Summary

Dielectric constant and power factor data on cellophane are given for a wide range of temperature and frequency. Anomalous dispersion and absorption are found and an hypothesis is advanced to explain the presence of orientation polarization in terms of the structure of the material.

Cellophane is found to have a dielectric con-

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[5] Kamerling and Smyth, THIS JOURNAL, **55**, 462 (1933).

[6] See Lipscomb, "Cellulose Acetate," Chap. II; Hausen, *Ind. Eng. Chem.*, **21**, 124 (1929).

[7] Sheppard, Nietz and Keenan, *Ind. Eng. Chem.*, **21**, 126 (1929).

stant nearly twice that of cellulose acetate. An explanation for this difference is suggested, based on their variation in chemical structure.

EAST PITTSBURGH, PENNA. RECEIVED MARCH 26, 1934

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

The Thermodynamic Dissociation Constant of Benzoic Acid from Conductance Measurements

BY FRANK G. BROCKMAN AND MARTIN KILPATRICK

In a contribution from this Laboratory[1] a tentative value of the thermodynamic dissociation constant of benzoic acid, obtained from conductance measurements, was reported. This paper reports a more accurate determination of this constant and compares the results with the Debye-Hückel theory.

Experimental Part

(*a*) **Alternating Current Bridge.**—The bridge used in these measurements differs in certain respects from those more recently described in the chemical literature[2] and a brief discussion of this apparatus follows.

The nucleus about which the bridge was built was a ratio box according to the design of Campbell and Shackelton.[3] The resistance boxes (carefully calibrated on a d. c. bridge by comparison with standards certified by the Bureau of Standards) were completely shielded, and resistors up to and including the 100-ohm decade were of bifilar construction. Resistances from 1000 to 10,000 ohms were obtained by the use of woven wire resistors which have the lowest time factor of any convenient resistors thus far produced. Although the ratio box is equipped with a Wagner grounding arrangement, this was not utilized in this investigation.[4] Any unbalance due to the power source was obviated by a carefully constructed power-transformer with balanced double shields. The shields surrounding the resistance boxes and the cell were removed to sufficiently great distances from the measured impedances so that the distributed capacities were negligible as shown by the absence of any variation of the measured resistance with a change in the frequency of the a. c. source from 1050 to 2730 c. p. s. In all instances the Grounded Point type bridge was employed. Complete shielding and the use of the Grounded Point type bridge much enhance the ease with which measurements can be made.

Resistance components were measured to 0.01 ohm. No resistances measured were less than 400 ohms. Electrolytic resistances greater than 10,000 ohms were shunted by a 10,000 ohm woven wire resistor and the electrolytic resistance computed.

(*b*) **Source of Alternating Current.**—The bridge was supplied alternating current from a shielded vacuum tube generator in which two type 112A tubes were used, the one as an oscillator and the other as an amplifier which serves to isolate the oscillatory system from the associated apparatus. The voltage applied to the bridge never exceeded 3 volts R. M. S. as measured by a thermocouple meter. Experimentation demonstrated that the energy dissipation corresponding to this voltage was low enough to prevent thermal changes in the measured resistance. All measurements were made at a frequency of 1050 c. p. s., but frequent checks at 2730 c. p. s. showed that no frequency error was to be found. Connections with the bridge were effected by a shielded two conductor cable.

(*c*) **Tuned Amplifier.**—The output of the bridge was fed through a shielded conductor pair to a shielded tuned two stage amplifier. Voltage amplification of a high order was obtained by feeding a type 36 screen grid vacuum tube through a tuned impedance into a type 37 triode, which in turn fed the head phones. The resonant frequency of the tuned circuit was determined by a series of fixed mica dielectric condensers.

(*d*) **Cell.**—The cell used in all measurements was a quartz-glass cell after the design of Shedlovsky.[5] The electrodes were platinized by adding successive thin layers of platinum black until the coating was just thick enough to prevent polarization with the most conducting solution to be measured. Such a condition was considered to be realized when, with the solution in the cell, no change in measured resistance occurred with a change in the frequency of the voltage source from 1050 to 2730 c. p. s. The cell was calibrated with a 0.01 "demal" solution of potassium chloride containing 0.74625_3 g. of potassium chloride in 1 kg. of water (weighed in air), which according to Parker and Parker[6] has a specific conductance of 0.0014078_9 ohm^{-1} cm.$^{-1}$ at 25°. On this basis the cell constant was 0.57386. The potassium chloride used was Kahlbaum, for analysis with guarantee, recrystallized twice from hot conductivity water and fused *in vacuo* before weighing.

(*e*) **Temperature Control.**—All measurements were carried out at 25 ± 0.003° by immersing the cell in a thermostat filled with transformer oil.

(*f*) **Conductivity Water.**—Pure water was prepared by redistillation from alkaline permanganate in a still similar to that due to Kraus and Dexter.[7] The conduc-

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[1] Kilpatrick and Chase, THIS JOURNAL, **53**, 1732 (1931).

[2] Jones and Josephs, *ibid.*, **50**, 1049 (1928); Shedlovsky, *ibid.*, **52**, 1793 (1930); Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

[3] For references see Behr and Williams, *Proc. Inst. Radio Eng.*, **20**, 969 (1932).

[4] Field, General Radio Experimenter, **4**, Jan., 1930, page 1; also, General Radio Experimenter, **6**, Sept., 1931, page 6.

[5] Shedlovsky, THIS JOURNAL, **54**, 1411 (1932).

[6] "I. C. T.," Vol. VI, p. 230.

[7] Kraus and Dexter, THIS JOURNAL, **44**, 2469 (1922).