[CONTRIBUTION FROM THE BUTTERFIELD CHEMICAL LABORATORY, UNION COLLEGE]

Studies on Silicic Acid Gels. XVI. The Effect of Radiant Energy upon the Time of Set

BY CHARLES B. HURD AND WINTERTON U. DAY[1]

Introduction

The effect or lack of effect of radiant energy upon the time of set of silicic acid gels has been mentioned a number of times in the literature. With the exception of the statement by Ray and Ganguly[2] that ultraviolet radiation from a mercury vapor tube definitely accelerated the setting of the gel, the statements concerning the effect of light have indicated that there is little if any effect. One of us has already made such a statement.[3] A reading of these statements concerning the negligible effects of light upon the time of set, except for that of Ray and Ganguly,[3] already mentioned, leads to the belief that the matter has not been carefully studied. Such a study, however, is relatively simple.

It would be rather surprising if a reaction of the type believed to occur in the setting of a silicic acid gel, namely, a reaction of condensation,[3] should be found to be affected noticeably by radiant energy. We have therefore made some careful experiments to detect the effect, if any. The results are reported herewith.

In addition, we have conducted one series of experiments with the General Electric Company's Recording Spectrophotometer, giving transmittance curves in terms of the age of the gel mixture.

Experimental

The gel mixtures were prepared by mixing solutions of sodium silicate, "E" brand Philadelphia Quartz Company, and acetic acid, in the manner described in former publications from this Laboratory,[4] using the same water thermostats and testing for time of set by the "tilted rod" method.

The mixtures were placed in 100-cc. Pyrex Griffin beakers in the thermostat. The volume in each beaker was 80 cc. Several duplicate samples were run in each case, the result given being the average. Three sources of radiation were used, a 100-watt Mazda bulb, a highvoltage iron spark, 18,000 volts, which gave lines from 4000 to 2200 Å, and a capillary mercury arc giving about the same range.

With the Mazda lamp, the samples run in the "light" were in clear beakers covered by clear watch glasses or cellophane covers. It made no difference whether glass or cellophane covers were used. For the iron and mercury radiation experiments, only cellophane covers were used. All runs in the "dark" were made in the same size beakers, heavily painted on the outside with aluminum paint. They were covered with watch glasses, heavily painted on the upper side with aluminum paint. The mixtures, of course, were exposed to light for a few seconds as they were being prepared.

The most essential factor here is the temperature. It is very easy, unless great care is exercised, to have the radiation received by the gel mixture cause a slight temperature rise. Since the time of set is very greatly affected by the temperature, this can be a real source of error. We have controlled the temperature in the following manner. The 100-watt Mazda lamp was suspended over the beakers in the thermostat and it was lowered to the position nearest to the beakers, which still gave no noticeable temperature rise on a sensitive thermometer. The thermometer may not be left in the mixtures while the radiation is being received, since the bulb intercepts sufficient radiation to show a false indication of a rise. The radiation was allowed to fall in the beakers and their contents, both the unpainted and the painted, for about five minutes. Then the light was turned off and the thermometer inserted in the gel mixtures.

We are confident that the Mazda lamp was as near to the contents of the beakers as possible without causing a rise in temperature of the contents. Water filters for shutting off a portion of the rays were considered, but not used. We are not so confident that we succeeded in having the mercury and the iron spark sources as close as they might have been without producing a temperature rise, since the apparatus was clumsy and much more difficult to adjust to the minimum distance. However, the mixtures were exposed to intense radiation through their cellophane covers.

At this time, it was possible to run one series of mixtures using the General Electric Company Recording Spectrophotometer,[5] in order to determine the transmission characteristics of these silicic acid gel mixtures during the process of gel formation. A copy of the curve is shown.

Data and Discussion

The data reported in Table I are the averages of six determinations each, the "dark" and "light" running side by side in the thermostat.

TABLE I

EFFECT OF RADIATION UPON TIME OF SET OF SILICIC ACID GEL MIXTURES

Type of radiation	Time of set in minutes "Light"	"Dark"	Temp. in °C.	Concentrations in gram moles or gram ions per liter SiO_2	Na^+	$HC_2H_3O_2$
Mazda	150	149	25.6	0.667	0.407	0.875
Mazda	1186	1182	25.6	.498	.305	2.570
Iron	151	152	25.6	.667	.407	0.875
Iron and mercury	95	95	29.0	.667	.407	.624

It is obvious from this that we have been unable to detect any significant effect of radiation upon the time of set, using radiation which does not incidentally produce a rise in temperature. At least in the case of the radiation in the visible spectrum, the Mazda lamp, we had all of the radiation possible without a temperature rise. The discrepancies in time are certainly below the possible experimental error in determination of times of set, namely, about 1%.

In Fig. 1 is given a tracing of the curves drawn by the Recording Spectrophotometer for a mixture containing SiO_2 0.67, Na^+ 0.41, and $HC_2H_3O_2$, 0.55 g. mole per liter. The room temperature was 26°. The curves were drawn at

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[1] Present address: Kimberly Clark Corporation, Neenah, Wisconsin.

[2] Ray and Ganguly, *J. Phys. Chem.*, **34**, 352 (1930).

[3] Hurd, *Chem. Revs.*, **22**, 403 (1938).

[4] Hurd, Raymond and Miller, *J. Phys. Chem.*, **38**, 663 (1934).

[5] We wish to thank the General Electric Company, and particularly Mr. J. I. Michaelson and Mr. W. R. Fanter, for their assistance.

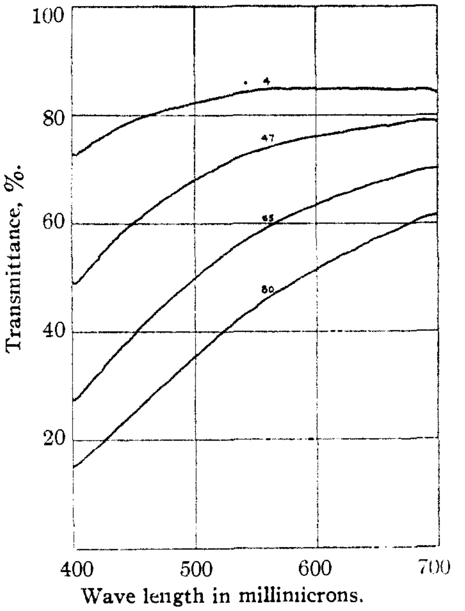

Fig. 1.—Transmittance of silicic acid gel mixtures as a function of wave length and age of sol.

four, forty-seven, sixty-five and eighty minutes after mixing, as indicated on the curve. The gel set in seventy-five minutes.

These transmittance curves are smooth, indicating no particularly strong absorption in any band. The curve of the mixture four minutes old shows the start of loss of the radiation of shorter wave length. This tendency increases with the age of the sol, until at age eighty minutes, which is five minutes after the gel has set, transmittance of radiation of 4000 Å. is only 0.15, while that of radiation 7000 Å. is 0.63 compared to a maximum of about 0.85 at the start, as shown on the four-minute curve. These results are probably due to the preferential scattering of radiation of smaller wave length. This scattering has been studied carefully by several investigators and the results reported.[6]

Summary

A study has been made of the effects of radiation upon the time of set of silicic acid gels, produced by mixing solutions of sodium silicate and acetic acid. Great care was taken that no measurable temperature change was produced by the radiation. Radiations from a Mazda lamp, a capillary mercury arc and an iron spark were used.

No significant effects of these types of radiation on the time of set were found.

A series of curves obtained with the Recording Spectrophotometer, showing the per cent. radiation transmitted by the sol are also given. The effect of age of the sol upon light transmitted is shown.

(6) Prasad, Mehta and Desai, *J. Phys. Chem.*, **36**, 1324 (1932).

Schenectady, N. Y. Received November 8, 1943

[Contribution from the Department of Chemistry at The Ohio State University]

Diolefins from Allylic Chlorides. II

By Albert L. Henne and Henry H. Chanan

We have shown[1] that two molecules of butadiene hydrochloride react with magnesium in ether to give a mixture of 1,5-diolefins, the composition of which remains the same whether the primary form of the halide, its secondary form, or the equilibrated mixture of both forms is used as the starting material. These results were in agreement with some of Young's observations[2] on allylic equilibria.

This method of synthesizing 1,5-diolefins is now extended to five allylic chlorides grouped in a variety of pairs. Allyl and methallyl chlorides which exist in only one form ($CH_2=CHCH_2Cl$ and $CH_2=C(CH_3)CH_2Cl$) were purchased. Piperylene hydrochloride which also exists in only one form ($CH_3CHClCH=CHCH_3$) was made by adding dry hydrogen chloride to commercial piperylene. Butadiene and isoprene hydrochlorides were made similarly from commercial butadiene or isoprene; they both exist in two forms, namely, $CH_3CHClCH=CH_2 \rightleftarrows CH_3CH=CHCH_2Cl$; and $(CH_3)_2C=CHCH_2Cl \rightleftarrows (CH_3)_2CClCH=CH_2$. All materials were supplied to us by a Research project of the American Petroleum Institute, directed here by Dr. C. E. Boord.

Experimentally, the condensations were carried out substantially as previously[1] described. Two different allylic chlorides were mixed in equimolecular proportion, and the mixture was added to magnesium turnings covered with dry ether. After completing the condensation and working up the products, a hydrocarbon fraction was obtained which amounted to about 35% of the quantity possible if pure allylic halides had been used and had condensed completely. It was, however, found more expedient to use the extremely impure materials obtained from a stream of hydrogen chloride through the commercial dienes and to discard from the condensation products all impurities, unreacted halides and resinified materials. From thirty to fifty moles

(1) Henne, Chanan and Turk, This Journal, **63**, 3474 (1941).

(2) Young, *ibid.*, **54**, 404 (1932); **58**, 104, 289, 441 (1936); **59**, 2051 2441 (1937); **60**, 847, 900 (1938).