The most important factor affecting the boiling points of these compounds is probably the dipole moment. Smyth[22] gives for the dipole moments of the three methylamines values of 1.23, 0.96 and 0.6, the more symmetrical amine having the lower amount. Trimethylamine, being the least firmly bound by dipole forces, therefore shows the lowest surface tension and can be more readily evaporated from the surface than would be expected on the basis of its molecular weight alone. The differences in the dipole moments of the three ethylamines is less pronounced, so that the effect of adding an ethyl group to the molecule predominates over the slight decrease in dipole moment and the boiling points fall in the normal order.

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Summary

1. The surface tensions of the methyl and ethylamines have been measured at 15, 25 and 35° with an accuracy of 0.5%.

2. The parachors do not indicate any structural abnormalities in the liquid state.

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[22] C. P. Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Company, New York, N. Y., 1931.

[CONTRIBUTION FROM THE PHILLIPS PETROLEUM COMPANY, RESEARCH DEPARTMENT]

The Reaction of Sulfur Dioxide with Olefins: the Ceiling Temperature Phenomenon

BY R. D. SNOW[1a] AND F. E. FREY

The liquid phase reaction of monolefins with sulfur dioxide to form polysulfones can be brought about by means of soluble catalysts, such as oxygen, peroxides, alkali nitrates, etc., or by exposure to actinic light.[1b] In the total absence of both light and catalysts apparently no reaction occurs.

In the course of an experimental study of this reaction embracing a variety of olefins and catalytic agencies, the reaction has been found, under certain conditions, to exhibit a steep negative temperature coefficient of rate. Raising the temperature through a few degrees, while maintaining a homogeneous liquid condition, suffices to virtually arrest reaction.

At the upper limiting temperature, or "ceiling temperature," the reaction between sulfur dioxide and some olefins was started or stopped repeatedly at will by alternately lowering and raising the temperature through an interval of one or two degrees. The ceiling temperatures found for the cases studied were as follows: propylene 87–89°, isobutylene 4–5°, 1-butene 63–66°, and 2-butene (*cis-trans* mixture) 43–45°. No change in the ceiling temperature was detected from start to completion of conversion in any experiment. Over a wide range of initial proportions of sulfur dioxide and a given olefin, the ceiling temperature was found to be independent of the relative concentration of the reactants. To our knowledge, no such sharp ceiling temperature effect has ever been reported for a homogeneous strictly chemical reaction. The closest analogy is found in the processes of photosynthesis and fermentation, both of which involve living cells.

Experimental Part

Since the temperature effect may be due to an unusual inhibition, pains were taken to prepare olefin reactants in high purity. The sulfur dioxide was the extra dry refrigerating grade. The Pyrex glass reaction tubes used were carefully cleaned, and reactant transfers were made in a vacuum system.

Isobutylene.—This olefin was selected as being particularly well suited for observing the ceiling temperature effect, since it did not react at room temperature, and when it did react it gave a heteropolymeric sulfone which was insoluble in sulfur dioxide and was easily observed by inspection. Three tubes were prepared. To one was added 1 cc. of 5% alcoholic lithium nitrate solution and to another the 3% hydrogen peroxide-paraldehyde-alcohol mixture used by Marvel.[2] The third tube was sealed without a catalyst (or alcohol addition) to study the photochemical reaction. A small quantity of resin (2–4%) formed in the tubes containing catalysts during the warming to room temperature after filling, but the reaction stopped well below room temperature; the solution cleared and no further resin formed during several hours. The tubes containing catalysts were then cooled slowly in a water-bath. The reaction in both started at +3.5–4° and was stopped at will by warming to 6°. The process of starting and stopping the reaction by alternately cooling and warming to these temperature levels was repeated several times during which possibly 20% conversion was obtained. During this time, the hydrogen peroxide catalyst became inactive and no further reaction occurred, even as low as 0°. The tube containing no catalyst was handled in a similar way. It was first exposed to bright sunlight at room temperature and no resin formed. On cooling slowly in the sunlight in a water-bath in a clear vacuum bottle, the resin formation began at about 4°, and took place quite rapidly at 3°. Once the mixture became cloudy, however, the reaction was slowed down by the screening of the light by the suspended resin. Here again, the reaction could be stopped by raising the temperature to 6° and started by cooling to 3.5–4°. All three tubes were then placed in a refrigerator and maintained at 8.5 to 9.5° for thirty-six hours, to see whether a slow reaction would occur slightly above the ceiling temperature. No additional resin formation could be detected. The tube containing lithium nitrate was again cooled, and the reaction began at 4°. After repeating the observation several times, the reaction

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[1a] Lt. Col. with Chemical Warfare, Edgewood Arsenal, Md.

[1b] For a more complete general discussion of the reaction and references to prior literature, see Frey and Snow, *Ind. Eng. Chem.*, **30**, 176 (1938).

[2] Marvel, THIS JOURNAL, **57**, 2312 (1935).

was allowed to go to completion at 2–3° to a solid white mass. In addition to demonstrating the sharp ceiling temperature effect, this experiment shows that the nitrate catalysts retain their activity over a comparatively long period of time. The sunlight exposure experiment also continued to show the same ceiling temperature as conversion proceeded with further exposure.

A series of tubes containing the catalyst and different concentrations of sulfur dioxide and isobutylene in the range of mole ratios, sulfur dioxide/isobutylene, of 0.5 to 8.0 were prepared and tested. No difference in the ceiling temperature could be detected throughout this range. Other experiments indicated that the ceiling temperature was unchanged by the presence of 25% by volume of isobutane, by water sufficient to form a second liquid phase, and by lower than normal concentrations of water, obtained by drying the isobutene and sulfur dioxide over phosphorus pentoxide and redistilling before mixing and reacting. The same ceiling temperature was also observed when sulfur dioxide prepared from c. p. sodium bisulfite was used. When 45% by volume of acetone was present, however, the same ceiling temperature effect was observed, but at about −5°.

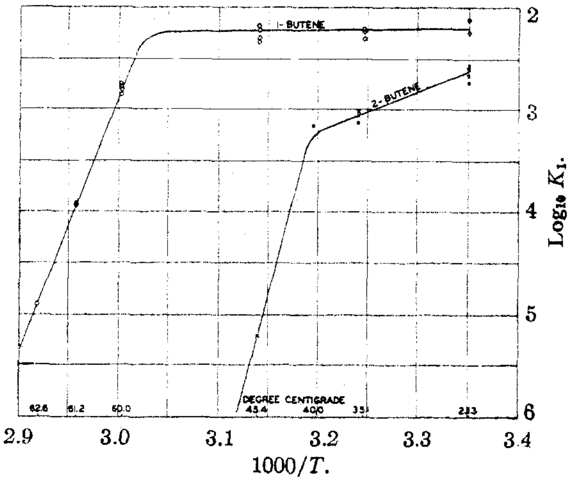

Fig. 1.—Effect of temperature on the reactions of butenes with sulfur dioxide.

Butenes.—1-Butene and 2-butene yield polysulfones soluble in sulfur dioxide, but with a limited excess of sulfur dioxide a viscous lower layer separates. 1-Butenes, using the technique just described, exhibited no heavy layer increase in a nineteen-hour exposure to bright sunlight at 77–93°. The tube was brought to 50–55° and reaction went to apparent completion in a day's further exposure. Similar sunlight experiments with 2-butene (*cis* plus *trans*) gave a threshold temperature slightly below 45°. Butene-2 with 0.07% silver nitrate catalyst in the dark gave no reaction in five hours at 45–47°. The temperature was dropped to 42°, whereupon reaction took place. On going to 45–47° no further reaction was observed in one hundred twenty hours.

Propylene.—With the sunlight technique propylene exhibited a ceiling temperature of 88°. In a one-gallon steel bomb with silver nitrate catalyst, the temperature rose spontaneously to 85° and no higher, falling off slowly as reaction approached completion.

Quantitative Experiments.—A quantitative study of the speed of the sunlight reaction near the ceiling temperature was then made for 1- and 2-butenes by the dilatometer method. Carefully measured quantities of gaseous butene and sulfur dioxide in the proportions of 8 moles of sulfur dioxide to 1 mole of butene were condensed in clean, evacuated dilatometer tubes. The large excess of sulfur dioxide was used in order that a clear single phase would be maintained at all times.

Before starting an experiment, the tubes were immersed slightly inclined from the horizontal in a large rectangular water-bath maintained constant to within 0.1° by means of a thermostat. As far as possible, all exposures were made between 10:00 A. M. and 2:00 P. M. in order to obtain as nearly constant intensity of sunlight as possible; nevertheless, some variation in intensity due to occasional clouds, haziness, and change in the angle of the sunlight were unavoidable. The rates of reaction were calculated from the contraction in volumes.

The temperature–rate data, plotted in Fig. 1, show sharp inflections at the ceiling temperature.

Discussion

It may be that, concurrently with polysulfone formation, there is formed a short-lived inhibitor by a reaction with a positive temperature coefficient of rate, which contrasts in this respect with the polysulfone-forming reaction. Possible mechanisms along more dynamic lines, however, deserve consideration. Each olefin species exhibited a characteristic ceiling temperature, despite variations in the catalytic agency and other conditions, and this suggests that the olefin itself plays an essential part in the inhibiting process. Furthermore, isobutylene has been shown[1b] to exhibit a strong inhibiting effect on 2-butene–sulfur dioxide reaction at a temperature above its own ceiling temperature. It is suggestive, too, that the ceiling temperature is lowest for these olefins most susceptible to acid-catalyzed polymerization. Further experimental study is indicated.

Summary

Simple olefin hydrocarbons and sulfur dioxide undergo a catalyzed reaction in a homogeneous liquid phase to form polysulfones of high molecular weight. As reaction temperature is elevated, the reaction was found to be suddenly arrested at a characteristic temperature level, but reaction sets in again upon lowering the temperature slightly below this level. This threshold has been designated the "ceiling temperature."

For any given olefin species the ceiling temperature is the same whether actinic light or catalytic substances are used to catalyze the reaction and despite variations in reactant proportions and purity.

A possible explanation is indicated.

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