

report by E. T. Lessig is now in press. With improved technique and proper allowance for the reverse reaction, this reaction now appears to be as satisfactory a unimolecular reaction as any yet reported.

The data at pressures above 100 mm. in the range 390 to 420° are well expressed by the formula

$$k = 3.85 \times 10^{14} e^{-54,800/RT}$$

Below 120 mm.  $k$  falls off, and at 20 mm. it has only about one-third of its high pressure value. In this low pressure region the reaction appears to be purely second order. Calculations indicate 22 squared terms on the basis of present theories. Theory I of Rice and Ramsperger [THIS JOURNAL, 49, 1617 (1927)] is not adequate to explain the facts. Temperature coefficients at the low pressures suggest that Kassel's Theory III [*J. Phys. Chem.*, 32, 225 (1928)] may fit better than Theories II or I.

The addition of nitrogen, and of hydrogen, causes the value of  $k$  at low pressures to *decrease*. According to present accepted theories the addition of foreign gases should increase the value of  $k$ . Unless some unexpected specific chemical effect exists, the results suggest that certain aspects of present theories of unimolecular reactions should be critically reassessed.

The influence of other foreign gases of increasing complexity is now being investigated.

LABORATORY OF PHYSICAL CHEMISTRY  
UNIVERSITY OF WISCONSIN  
MADISON, WISCONSIN

RECEIVED MAY 9, 1932  
PUBLISHED JUNE 6, 1932

E. L. VERNON  
FARRINGTON DANIELS

---

#### THE EINSTEIN RELATION AND TEMPERATURE COEFFICIENT IN THE PHOTOBROMINATION OF CINNAMIC ACID

Sir:

Exact measurements on the photobromination of cinnamic acid, now in progress, show clearly that it is possible to obtain a quantum efficiency of 1 and a temperature effect of zero in agreement with simple photochemical theory, when accompanying thermal reactions are suppressed. They show, too, how the temperature coefficient of the total reaction can vary with the concentration.

The experiments were carried out in a quartz cell of 15-cc. capacity. Light of 4358 Å. was isolated from the spectrum of a capillary quartz mercury arc by means of a monochromator. The change in bromine concentration after fifteen minutes' illumination was measured and compared with the change in the control kept in the dark. The concentration of cinnamic acid was the same in all cases.

The results are summarized in the accompanying figure where  $\Phi$ , the number of molecules of bromine consumed per quantum of light absorbed, is plotted against the concentration of bromine. This concentration is expressed in moles of bromine per liter of 0.00567 molar cinnamic acid in carbon tetrachloride. The reaction is a chain reaction, the products of the bromination apparently contributing some of their energy to activate new molecules of bromine.

The striking regularity with which  $\Phi$  decreases as the dilution increases suggests that the energized products of the reaction gradually lose their activation by collision with the molecules of carbon tetrachloride. At infinite dilution the deactivation of products by the solvent should be so complete that no chain reaction is possible. Under these conditions, where secondary thermal reactions are eliminated, the quantum yield should be exactly 1. Extrapolation of the experimental curves to infinite dilution shows that this prediction is correct.

Furthermore, at infinite dilution where the reaction is purely photochemical, the temperature effect should be zero. Again the graphs support this prediction in a striking manner. The curves at 30 and 0° both extrapolate, within the limit of experimental error, to the same value of  $\Phi$ , namely 1.

In the more concentrated solutions the reaction is about eight times as fast at 30 as at 0°. The ratio of rates for a 10° difference in temperature is 1 at infinite dilution and increases to a limiting value of 2 in the more concentrated solutions. This value is in agreement with that of ordinary thermal reactions.

Experimental measurements and calculations are being continued.

LABORATORY OF PHYSICAL CHEMISTRY  
UNIVERSITY OF WISCONSIN  
MADISON, WISCONSIN

RECEIVED MAY 9, 1932  
PUBLISHED JUNE 6, 1932

WALTER H. BAUER  
FARRINGTON DANIELS

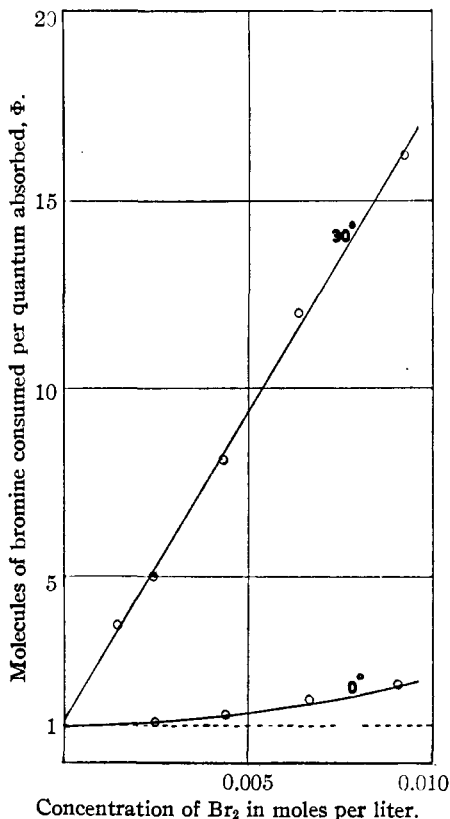


Fig. 1.—Photobromination of cinnamic acid in carbon tetrachloride.