weights. This shift of the intrinsic viscosity–molecular weight curves is summarized graphically in Fig. 6. The theoretical expressions of Huggins[16] and of Hulburt, Harmon, Tobolsky and Eyring[17] represent the viscosity as proportional to inverse powers of the weight per chain atom so in this respect at least they are approximately valid.

It is interesting to note that of the various theories only that of Haller[18] predicts accurately the dependence of the viscosity on the two-thirds power of the molecular weight.[19]

Acknowledgments.—The authors wish to thank Dr. Paul J. Flory and the Esso Laboratories for furnishing the three fractions of polyisobutylene; the Firestone Tire and Rubber Company, in particular Dr. J. H. Dillon, for furnishing the rubber samples; Professor Arthur V. Tobolsky for several helpful discussions; and Professor Hugh S. Taylor for his generous interest and valuable advice.

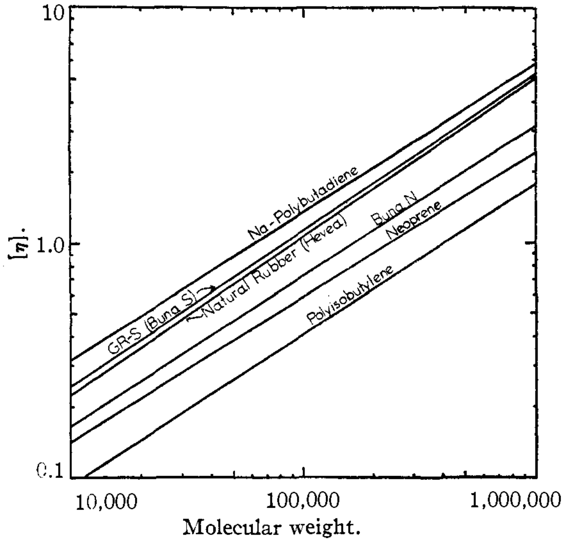

Fig. 6.—Viscosity–molecular weight relations for toluene solutions of various polymers.

Summary

Measurements on six different high polymers have shown that the intrinsic viscosity of the solutions depends on approximately the two-thirds power of the molecular weight. Dependence of the viscosity on the weight per chain atom of the polymer is indicated.

LOS ANGELES 24, CALIFORNIA RECEIVED APRIL 20, 1948

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[16] M. L. Huggins, *J. Phys. Chem.*, **42**, 910 (1938); **43**, 439 (1939); *J. Appl. Phys.*, **10**, 700 (1939).

[17] H. M. Hulburt, R. A. Harmon, A. V. Tobolsky and H. Eyring, *Ann. N. Y. Acad. Sci.*, **44**, 371 (1943).

[18] W. Haller, *Kolloid Z.*, **56**, 257 (1931).

[19] Since this paper was first submitted to the Editor of The Journal, two new theories of viscosity have appeared, one by P. Debye and A. M. Bueche (*J. Chem. Phys.*, **16**, 573, 1948) and one by J. G. Kirkwood and J. Riseman (*ibid.*, **16**, 565, 1948). On preliminary inspection, it seems that our data are entirely consistent with these new theories, but rather than further delay publication of these results, we postpone a detailed discussion to a subsequent paper.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Kinetics of Semicarbazone Formation with Para Substituted Acetophenones[1]

BY ROBERT P. CROSS AND PAUL FUGASSI

The kinetics of the reactions of *d*-carvone with semicarbazide and other carbonyl reagents have been investigated previously by Stempel and Schaffel[2] and Mariella[3] using a polarimetric method. It is the purpose of this investigation to examine the kinetics of semicarbazone formation with para substituted acetophenones by a competitive method in which *d*-carvone and acetophenone react simultaneously with semicarbazide, present in sufficiently low concentration that the carbonyl reagent distributes itself between the two ketones. The extent of reaction of the *d*-carvone is determined polarimetrically.

Experimental Technique

Preparation of Compounds.—*d*-Carvone was obtained from Magnus, Mabee and Reynard. It was purified by preparing the solid hydrosulfide.[4,5] After several recrystallizations of the hydrogen sulfide compound, *d*-carvone was recovered by treating the compound with concentrated sodium hydroxide solution and steam distilling the mixture. Following extraction of the carvone with ether, the extract was vacuum distilled several times and a fraction collected boiling at 78° at 3 mm. The physical constants of our sample agreed with those found by Stempel and Schaffel.[2] Semicarbazide hydrochloride (an Eastman Kodak Co. product) was recrystallized from hydrochloric acid solution. Acetophenone was purified by the method of Flexser, Hammett and Dingwall.[6] The sample of acetophenone used boiled at 193° at 743 mm. *p*-methoxyacetophenone and *p*-chloroacetophenone were prepared by the method of Adams and Noller.[7] The

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[1] Abstracted from the thesis submitted by Robert P. Cross on August 12, 1947, to the Committee on Graduate Degrees, Carnegie Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Science. Presented before the Division of Physical and Inorganic Chemistry at the 113th meeting of the American Chemical Society at Chicago, April, 1948.

[2] Stempel and Schaffel, THIS JOURNAL, **66**, 1158 (1944).

[3] Mariella, Thesis, Carnegie Institute of Technology, October 4, 1945.

[4] Wallach, *Ann.*, **305**, 224 (1889).

[5] Hooper, Macbeth and Price, *J. Chem. Soc.*, 1147 (1934).

[6] Flexser, Hammett and Dingwall, THIS JOURNAL, **57**, 2103 (1935).

[7] Adams and Noller, "Organic Synthesis," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 109–111.

former compound melted at 38° and the latter boiled at 85° at 5 mm. *p*-Methyl and *p*-bromo acetophenone were Eastman chemicals. The *p*-bromoacetophenone was recrystallized several times from hot ethanol to give a sample with a melting point of 50.5°. *p*-Methylacetophenone was distilled several times at reduced pressure. The fraction used boiled at 94° at 10 mm.

Physical Measurements.—Rotations were measured with a Hilger M-8 polarimeter using the mercury green line at 5461 Å. Readings could be made to 0.01°. The polarimeter tube, 5 decimeters long, was provided with a water jacket, insulated with magnesia–asbestos, through which thermostatted water was pumped. Beckmann thermometers were placed at the inlet and outlet water connections and the thermostat adjusted so that the mean temperature of the polarimeter tube was 30, 40 or 50°.

Two general types of experiments were made. In the first type of experiment *d*-carvone reacted with semicarbazide, while in the other type *d*-carvone and an acetophenone reacted with semicarbazide. For the experiments with carvone alone the reactants were brought to the temperature of the experiment and mixed in a volumetric flask kept at the temperature of the experiment. Sufficient solvent (83% ethanol in water) was then added so that the starting concentrations of semicarbazide, semicarbazide hydrochloride and *d*-carvone were all equal to 0.015 mole/liter. After thorough mixing, the solution was transferred to the polarimeter tube and the rotations measured at definite time intervals taking zero time as the instant when the reactants were mixed. In the second type of experiment the reactants were mixed in a volumetric flask kept at the temperature of the experiment and sufficient 83% ethanol added so that the starting concentrations of carvone, substituted acetophenone, semicarbazide, and semicarbazide hydrochloride were all equal to 0.015 mole/liter. After mixing the solution was allowed to remain in the thermostat for a period of approximately twenty, ten or five hours depending on whether the temperature of the experiment was 30, 40 or 50°, respectively. These periods of time correspond to the time interval necessary for 99% of the reaction to take place when carvone alone is reacted with semicarbazide.

Calculation of Velocity Constants

In the experiments with *d*-carvone a first order plot of $-\log (1 - f)$ against time fits the experimental data for values of f (fraction decomposed) up to 0.5. For the experiments at 30°, f values of about 0.5 were the highest that could be obtained in reasonable reaction times. At 50°, however, f values up to 0.93 were obtained. For the higher temperature experiments the experimental points corresponding to f values greater than 0.5 were above the straight line first order plot. The experimental points at these higher values of f diverged more and more from the first order line as f increased in value. The direction of the drift indicates that in the later stages the reaction is approaching zero order. However, in view of the fact that we are dealing with a complex system and a reversible reaction in which the points obtained at low f values should be stressed to minimize the effect of the reverse reaction, it does not seem desirable to stress fitting of the experimental points at high f values. Consequently, the experimental data for the experiments with *d*-carvone alone were calculated on the basis of the first order equation, $kt = -2.3 \log(1-f)$.

In the experiments where two ketones reacted simultaneously with semicarbazide, it appears possible to ignore the reverse reactions. Experimentally it is known that the semicarbazones of either carvone or acetophenone do not react appreciably, in the time intervals used here, with acetophenone or carvone, respectively. The equilibrium constant for the formation of carvone semicarbazone is known to be large. The equilibrium constant for the formation of acetophenone semicarbazone is also believed to be large. A value for the latter equilibrium constant is not cited because in the periods of time (weeks) necessary for equilibrium the solutions darken even if protective nitrogen atmospheres are employed. The darkening of the solution interferes somewhat with the measurement of the rotation and might be indicative of slow side reaction which would influence the equilibrium but would have little or no influence on the kinetics because of their slowness. In the kinetics measurements reported here all solutions were colorless at the end of the time intervals used. Until the origin of the darkening of the solutions is discovered it does not seem desirable to list numerical values for the equilibrium constant. With regard to substituted acetophenones it is fairly certain that the substitution of groups on acetophenone will change the numerical values of the equilibrium constant for semicarbazone formation but will not change its order of magnitude.

Accordingly we assume following Grazzi[8] that each ketone follows a rate equation of the form

$$\mathrm{d}x_i/\mathrm{d}t = k_i(a_i - x_i)f(x_i)$$

where a_i is the starting concentration of the ketone, x_i the concentration of ketone which has reacted at time t, and $f(x_i)$ a function of the concentrations of all the other reactants involved. Under the experimental conditions employed it is assumed that $f(x_i)$ has the same value for all ketones so that we may write

$$\frac{\mathrm{d}x_1}{k_1(a_1 - x_1)} = \frac{\mathrm{d}x_2}{k_2(a_2 - x_2)}$$

where the subscripts 1 and 2 refer to *d*-carvone and the other ketone, respectively. Integration of this equation together with the use of the boundary condition that at zero time the concentrations of *d*-carvone, other ketone, semicarbazide and semicarbazide hydrochloride are all equal gives the equation

$$k_2 = k_1 \frac{\log f'}{\log (1 - f')}$$

where f' is the fraction of *d*-carvone which has reacted at the given time interval with the other ketone present, relative to the amount of reaction undergone by *d*-carvone at infinite time when the other ketone is absent.

Experimental Data

For the experiments with *d*-carvone alone the following average values of k representing the

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[8] Grazzi, *Gazz. chim. ital.*, **38**, 32 (1908); **40**, 140 (1910)

mean of three determinations at each temperature were obtained: 30°, 3.74×10^{-3}min.$^{-1}$; 40°, 7.68×10^{-3}min.$^{-1}$; and 50°, 1.6×10^{-3}min.$^{-1}$.

With experiments using two ketones a minimum of five experiments were made at each temperature for each ketone. The average values of the velocity constants were plotted on a typical Arrhenius plot and the constants in the Arrhenius equation, $\log k = A - \frac{E_A}{2.3RT}$, were evaluated. E_A is the energy of activation. The values of the constants are collected in Table I.

TABLE I

ARRHENIUS EQUATION CONSTANTS

Ketone	A, min.$^{-1}$	E_A, cal.
p-Methoxyacetophenone	−0.57	4,000
p-Methylacetophenone	1.38	6,540
Acetophenone	2.33	7,800
p-Chloroacetophenone	4.44	10,330
p-Bromoacetophenone	5.00	11,040

Discussion

Reference to Table I indicates that the activation energy of semicarbazone formation varies with the nature of the substituting group in the para position and that in order of decreasing activation energy the substituting groups would fall in the sequence Br > Cl > H > CH_3 > CH_3O. It is obvious that the above sequence is the same one that would be obtained if the substituting groups were arranged in the order of their ability to withdraw electrons from the ring. As semicarbazone formation only involves the carbonyl group, it is apparent that the charge density on the carbon atom is the determining factor and that the influence of the substituting group is due to its effect upon the charge density of the carbonyl carbon. A number of reactions are influenced by substitution in this manner and to these Hammett has applied the equation, $\log k - \log k^0 = \rho\sigma$. In this equation k is the rate constant for the substituted compound, k^0 is the rate constant for the unsubstituted compound, σ is a constant depending upon the nature of the substituting group, and ρ is a constant characteristic of the reaction. If the values of σ evaluated by Hammett are used, a plot of log k *versus* σ gives a straight line of slope ρ. The slope and value of ρ for the semicarbazone formation turns out to be 0.91. Another method of illustrating the effect of the substituting groups is to plot log $K_{(\text{dissociation})}$ which is proportional to the free energy of dissociation of the corresponding substituted benzoic acid, against the energy of activation of the corresponding substituted ketone. Such a plot is illustrated in Fig. 1. Reference to Fig. 1 shows that the carbonyl carbon having the highest charge density as exemplified by the highest positive free energy of dissociation of the corresponding substituted benzoic acid also has the lowest activation energy. This behavior suggests that the rate-determining step in the semicarbazone reaction is a reaction involving the transfer of a proton to the reaction complex. However, the suggested mechanism for semicarbazone formation is quite complicated as will be seen by reference to Stempel and Schaffel.[2] Since for such a mechanism the experimental velocity constant is the product of the velocity constant of the rate determining step and a number of equilibrium constants, the activation energy obtained from the experimental velocity constant is a composite term in the sense that it includes heats of reactions for the various equilibrium reactions. Consequently the effect of a substituting group might be due in part to changes in heats of reactions caused by such groups.

Acknowledgment.—The authors wish to thank Dr. A. A. Orning, Dr. Gerson S. Schaffel and Dr. Guido H. Stempel for their comments and suggestions.

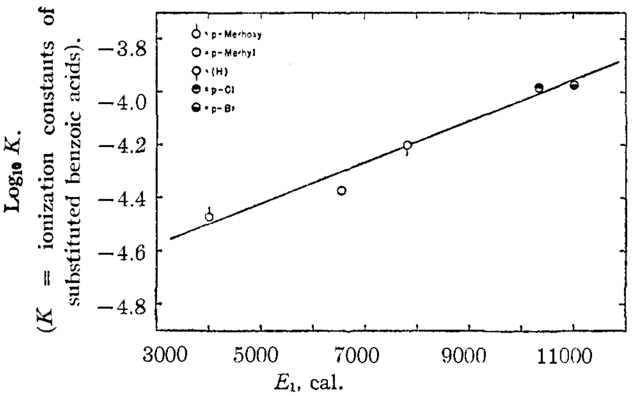

Fig. 1.—Energy of activation for semicarbazone formation of acetophenone series.

Summary

1. The rate of semicarbazone formation of acetophenone and substituted acetophenones has been determined by a competitive method using *d*-carvone as the competing ketone.

2. The effect of para substitution upon the experimental activation energy of the semicarbazone reaction with acetophenone is given by the sequence, Br > Cl > H > CH_3 > CH_3O, with *p*-bromoacetophenone showing the highest activation energy.

3. It is suggested that the rate determining step is a reaction involving transfer of a proton to the reaction complex.

PITTSBURGH, PA. RECEIVED APRIL 5, 1948