either by cosmic ray bursts, local radioactivity or catalytic material. They used a round Pyrex flask filled with hydrogen, and admitted fluorine through a copper tube positioned in the center of the flask by means of a rubber stopper. Because of this inconsistency with our results we recently duplicated exactly the Eyring–Kassel experiment and found that *pure* fluorine gas invariably ignites at the tip of the copper tube in a hydrogen atmosphere and burns with a pale blue flame. Evidently their "fluorine" consisted of oxygen (with or without HF) due to the presence of moisture in their electrolytic fluorine cell. The explosions they observed took place whenever sufficient fluorine was generated to reach the explosive limit of whatever mixture was present.

Agreeing, however, with Eyring and Kassel's assumption that the homogeneous reaction between the two gases requires considerable activation energy, we were able to premix them, at atmospheric pressure, in the whole range from 100% H_2 to 100% F_2 by (a) eliminating impurities in the gases, particularly HF, (b) avoiding the presence of all transition metals and their compounds (*i.e.*, particularly Cu, Fe and Ni) in the mixing chamber, and (c) precooling both gases to 90°K. After mixing under the above conditions the gases could be warmed up to 195°K. in Pyrex glass apparatus without ignition. We have also been able to burn H_2–F_2 mixtures without explosions or detonations in the range of 6 to $\cong$ 25 vol. % F_2, from both Pyrex glass and magnesium metal tips for periods of $\simeq$ 0.5 hr. or longer at atmospheric pressure. In contrast to the diffusion flame, the premixed gases burn as a very pale pink but clearly defined cone with a *burning velocity far in excess of any known flame.* The velocity was measured by the cone height method in the range of 0.1 to 0.4 of stoichiometric and the results shown in Fig. 1. The H_2–O_2 flame is the fastest flame known to date, with a maximum laminar burning velocity of 900 cm./sec. at 300°K., close to the stoichiometric point. In order to compare both flames at the same initial conditions (*i.e.*, 90°K.), in the same range of Reynolds numbers (*i.e.*, 10–15 × 10^3), and with the same type apparatus, Mr. C. S. Stokes, of our laboratory, measured the burning velocities of various H_2–O_2 mixtures both at 90° and at 300°K.; his results at 90°K. are also given in Fig. 1. A comparison shows that the H_2–F_2 flame burns about ten times faster than the H_2–O_2 flame; thus at 0.33 of stoichiometric the velocities are 1750 and 160 cm./sec., respectively.

Another characteristic of this flame is the high pressure exerted by the flame front on the uncombusted gases. In the fastest and hottest flames known to date,[7] *i.e.*, in the H_2–O_2 and the C_2H_2–O_2 flames, the maximum pressure exerted close to the stoichiometric point is only 2.2 and 4.1 mm. Hg, respectively. The values for the H_2–F_2 flame rise rapidly from 5 mm. at 0.1 to about 100 mm. Hg at 0.4 of the stoichiometric point.

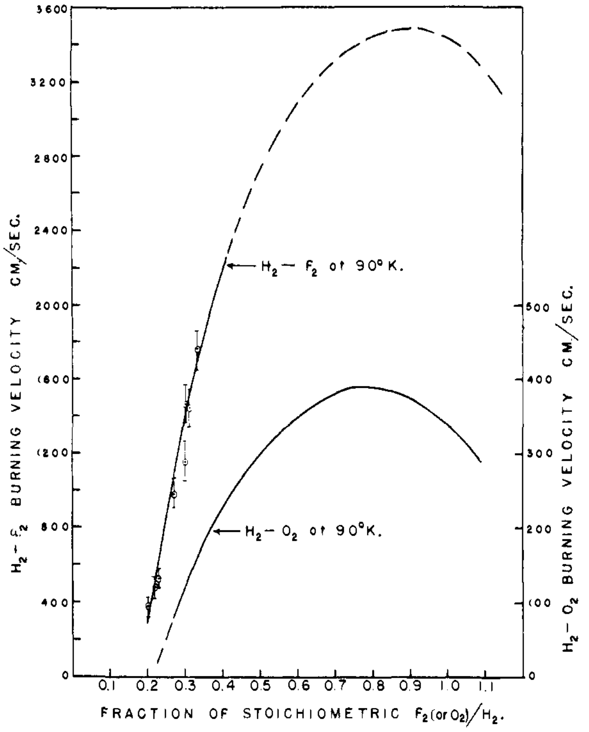

Fig. 1.—Burning velocities of H_2–F_2 and H_2–O_2 flames at 90°K.

We have not been able as yet to approach the stoichiometric point, due to the extreme detonation sensitivity of these mixtures, coupled with rapid increase in both velocity and pressure as the F_2 content is increased. The velocity of the fastest burning mixture (close to the stoichiometric point on the H_2-rich side) can be extrapolated to $\simeq$3500 cm./sec. at 90°K. and a preliminary estimate would place the burning velocity at room temperature at about 10,000 cm./sec.

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[7] See B. Lewis and G. von Elbe, "Combustion, Flames and Explosions of Gases," Academic Press, Inc., New York, N. Y., 1951, p. 266.

The Dissociation of Sodium Acetylide

BY S. A. GREENE[1]

RECEIVED APRIL 25, 1955

The decomposition of sodium acetylide to yield acetylene and sodium carbide has been reported by several investigators.[2] Decomposition was reported to take place between 190 and 220°. Nieuwland and Vogt[3] have noted the loss of acetylene from sodium acetylide at about 160° under partial vacuum. We have investigated this reaction between 100 and 183° and found it to be a heterogeneous equilibrium which may be represented as

$$2NaC_2H \rightleftarrows Na_2C_2 + C_2H_2 \qquad (1)$$

Experimental

Ten grams of sodium acetylide was placed in a glass bulb and immersed in an oil-bath which was thermostated to ±0.05°. The compound analyzed 98% pure, the impurities being sodium oxide, hydroxide and carbonate. The bulb

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[1] Aerojet General Corp., Azusa, Calif.

[2] R. de Forcrand, *Compt. rend.*, **120**, 1215 (1895); C. Matignon, *ibid.*, **124**, 775 (1897); H. Moissan, *ibid.*, **136**, 1217, 1522 (1903).

[3] J. A. Nieuwland and R. R. Vogt, "The Chemistry of Acetylene," Reinhold Publ. Company, New York, N. Y., 1945, p. 44.

was connected to a manometric system which included an acetylene reservoir. Pressures, read by means of a cathetometer to ±0.05 mm., were reduced to standard barometric conditions. Temperature was established with a mercury thermometer which had been calibrated by the National Bureau of Standards and could be read to ±0.05°. The powdered sample was outgassed *in situ* under moderate vacuum at 100°. After adjusting the bath to the desired temperature, equilibration took place in from 1 to 3 hours.

The results are shown in Fig. 1. The point represented as a solid circle was approached from both the high and low pressure side, the two readings agreeing to within 1%. All other points were approached from the low pressure side. The dissociation pressures are given by

$$\log_{10} P = 8.538 - 2749/T \qquad (2)$$

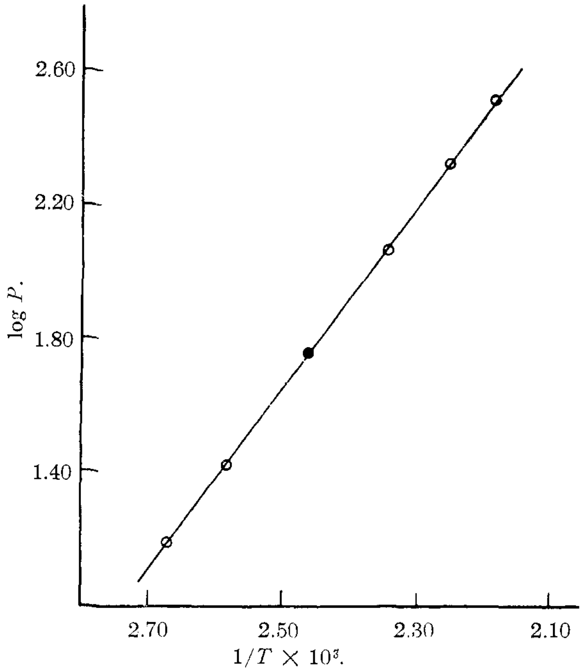

Fig. 1.—Equilibrium pressures (mm.) of acetylene over sodium acetylide and carbides.

The heat of dissociation derived from equation 2 is +12.6 kcal. The heat of dissociation computed from standard heats of formation[4] of the reactants and products at 18° is

$$\begin{array}{cccc} 2NaC_2H \rightleftharpoons & Na_2C_2 + & C_2H_2 & \underline{\Delta(\Delta H^\circ)} \\ 2(25.1) & (4.1) & (54.3) & 8.2 \text{ kcal.} \end{array}$$

The standard heats of formation of the solids are derived from measurements of heats of solution.

[4] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publ. Corp., New York, N. Y., 1936, pp. 144–145; P. W. Wagman, J. E. Kilpatrick, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 467 (1945).

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The System of *p*- and *o*-Ethylacetanilides

BY GENNADY M. KOSOLAPOFF

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Probably the most convenient route to many of the derivatives of ethylbenzene lies through the intermediates of *o*- and *p*-nitroethylbenzenes and the corresponding amines. The acetyl derivatives of the latter afford a convenient check on the purity of the isomers, and the quality of the subsequent products. However, the existing data in the literature concerning these acetyl derivatives must be regarded as extremely scanty, since only the individual melting points are recorded[1–3] and no quantitative data may be found about their solubilities.

It was felt that the determination of the phase diagram of the two acetyl derivatives and the determination of their solubilities in water would be of assistance in filling this informational gap.

The necessary nitro and amino compounds were prepared in a manner similar to that employed by Birch, *et al.*[1] However, it was observed that if the crude nitroethylbenzenes are steam distilled, prior to the vacuum fractionation, no difficulty in respect to decomposition is observed even if the pot temperature is maintained at well above 150° for many hours (usually 24–30 hours) during the fractionation. The amines were acetylated conventionally with acetic anhydride in sodium acetate buffer and the substances were recrystallized: the *ortho* isomer from water, the *para*-isomer from dilute alcohol.

While the method of cooling curves gave good results with the pure substances and with their mixtures at the extremities of the composition curve, it was unsatisfactory in the mid-portion of the diagram owing to very severe supercooling and glass formation. For this reason, the phase diagram of *o*- and *p*-ethylacetanilides was explored by the method of capillary melting points, only the pure isomers and their 10:90 mole % mixtures being further verified by the cooling curve method.[4]

The phase diagram of the system is that of solid solution type with a eutectic as shown in Table I. The temperatures given are corrected.

Solubilities of the two isomers in distilled water were determined at 30° and at 50°. It is to be noted that the *p*-isomer shows a decidedly higher temperature coefficient of solubility than does the *o*-isomer. The determinations were made conventionally by equilibration of the powdered solids

TABLE I

THE SYSTEM OF *o*- AND *p*-ETHYLACETANILIDES

o-Isomer, mole %	Liquidus, C.	Solidus, C.	*o*-Isomer, mole %	Liquidus, C.	Solidus, C.	Solubility, g./100 ml. soln. *o*-Isomer	Solubility, g./100 ml. soln. *p*-Isomer
						30°	
100	112.9	112.9	40	67.5	65.0	0.4192	0.1168
90	109.5	95.0	30	74.0	67.4		
80	104.8	84.0	20	84.0	74.0	50°	
70	97.8	75.0	10	90.5	82.5	.5256	.2276
60	89.0	69.5	0	94.8	94.8		
50	79.2	66.0	38.8	64.8	64.5		

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[1] S. F. Birch, R. A. Dean, F. A. Fidler and R. A. Lowry, THIS JOURNAL, **71**, 1362 (1949).

[2] W. J. Hickinbottom, *J. Chem. Soc.*, 64 (1927).

[3] J. v. Braun, O. Bayer and G. Blessing, *Ber.*, **57**, 398 (1924).

[4] In the determination of the final melting temperatures (liquidus line) it was convenient to observe the appearance of the reflection of the translucent specimen in the capillary as it appeared on the mercury bulb of the thermometer, the incident light being directed through the specimen. The instant of disappearance of the trace of haze was much more readily observable in this manner than it was by direct observation of the specimen.