a peak at 420 mμ which may be attributed to the *trans*-form of the dye, as has been suggested for other azo dyes.[3-5] The absorption at 420 mμ dropped after exposure of the solution to light and a new peak began to develop at 380 mμ. In addition, the original band shifted to somewhat longer wave lengths. These changes are due to the production of the *cis*-isomer.[3-5] The double-banded curve shown in Fig. 1 may be ascribed to the existence of both *cis*- and *trans*-forms in the steady state mixture maintained in the presence of light.

Almost identical spectra were obtained for the dye dissolved in pyridine which, like dimethylformamide, is an aprotic solvent. In contrast, in a series of primary alcohols, solvents with proton-donor character, the concentration of *trans*-isomer in the steady state (at a given light intensity) was always greater than in the aprotic solvents, and, furthermore, increased as one went downward in the series from decanol to ethanol. Such behavior is consistent with the suggestion that the catalysis of the *cis–trans* transformation is directly dependent on the proton-donor ability of the solvent and that the intermediate complex is ionic.[3,5] It also becomes apparent why this azo compound exists entirely in the *trans* form in aqueous solutions.

The kinetics of the dark reaction, the *cis–trans* isomerization, were followed quantitatively in dimethylformamide and in pyridine, respectively. In each case, a first-order rate law was followed (Fig. 2). Rate constants, k, computed from the slopes of the lines in Fig. 2, are listed in Table I. From the increase in rate with increasing temperature, the free energy $\Delta F^{\ddagger}$, enthalpy $\Delta H^{\ddagger}$, and entropy $\Delta S^{\ddagger}$, of formation of the activated complex were computed.[7] The magnitudes of these quantities are close to those observed in the *cis–trans* isomerization of other azo dyes.[3] Evidently the mechanism of the transformation is the same in all cases.

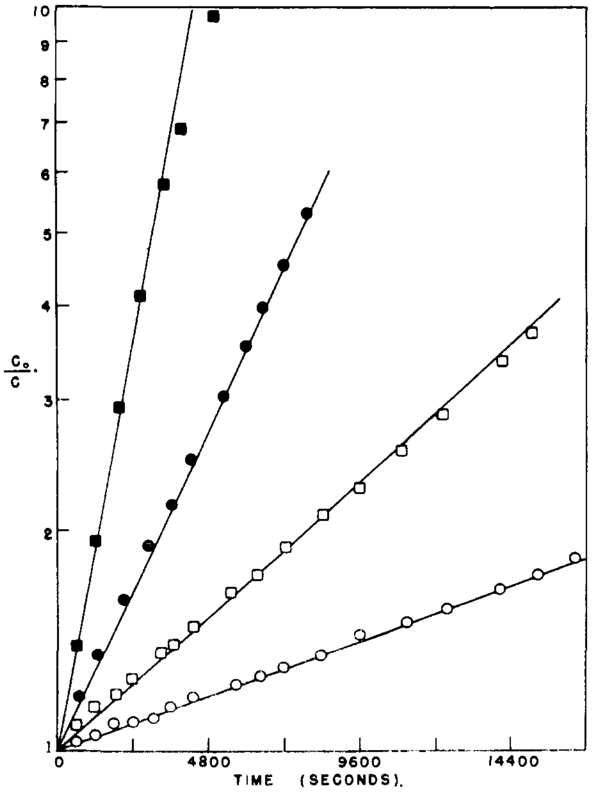

Fig. 2.—Rate of *cis–trans* conversion of 4-(*p*-dimethylaminobenzeneazo)-phenylmercuric acetate in N,N'-dimethylformamide at 19.4°; ○, in N,N'-dimethylformamide at 19.4°; ●, in N,N'-dimethylformamide at 35.4°; □, in pyridine at 19.4°; ■, in pyridine at 35.4°.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE *cis–trans* TRANSFORMATION OF 4-(*p*-DIMETHYLAMINOBENZENEAZO)-PHENYLMERCURIC ACETATE

Solvent	k, sec.$^{-1}$ × 10^5 At 19.4°	At 35.4°
Pyridine	8.81	53.3
N,N'-Dimethylformamide	3.68	21.0

TABLE II

"THERMODYNAMIC" QUANTITIES FOR THE *cis–trans* TRANSFORMATION OF 4-(*p*-DIMETHYLAMINOBENZENEAZO)-PHENYLMERCURIC ACETATE AT 19.4°

Solvent	$\Delta F^{\ddagger}$ (cal./mole)	$\Delta H^{\ddagger}$ (cal./mole)	$\Delta S^{\ddagger}$ (e.u.)
N,N'-Dimethylformamide	23,000	18,900	−14.0
Pyridine	22,500	19,600	−9.9

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(7) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 95.

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The Premixed Hydrogen-Fluorine Flame and its Burning Velocity

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RECEIVED JUNE 3, 1955

In recent years we have studied various high temperature flames, among them the H_2–F_2 flame.[1-3] This was a diffusion type flame, with pure F_2 burning in excess H_2.

The literature data on the possibilities of premixing the two gases are conflicting. We observed a number of years ago[4] that the flame is self-igniting whenever pure fluorine gas emerges from a copper tip into a H_2 atmosphere.[2,3] Our recent attempts to mix the two gases in a steel chamber cooled to −78° at linear velocities up to 100 m./sec. invariably led to self-ignition in the chamber.[5]

On the other hand, Eyring and Kassel[6] described the ignition- and explosion-free mixing of the two gases, in the whole range of 100% H_2 to 100% fluorine at room temperature, with only occasional explosions, which they believed were initiated

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(1) R. H. Wilson, Jr., J. B. Conway, A. Engelbrecht and A. V. Grosse, THIS JOURNAL, **73**, 5514 (1951).

(2) W. S. Benedict, B. W. Bullock, S. Silverman and A. V. Grosse, *J. Opt. Soc. Amer.*, **43**, 1106 (Nov. 1953).

(3) R. H. Wilson, Jr., J. B. Conway, A. Engelbrecht and A. V. Grosse, *Natl. Bur. Stand. Circ.* **523**, 111 (March 10, 1954).

(4) H. Priest and A. V. Grosse, *Ind. Eng. Chem.*, **39**, 431 (1947).

(5) R. H. Wilson, Jr., J. B. Conway, A. Engelbrecht and A. V. Grosse, O.N.R. Report "The Hydrogen-Fluorine Torch," Aug. 1, 1951; see also O.N.R. Final Report, Contract N9-onr-87301 by J. B. Conway and A. V. Grosse, July 1, 1954.

(6) H. Eyring and L. Kassel, THIS JOURNAL, **55**, 2796 (1933).

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.

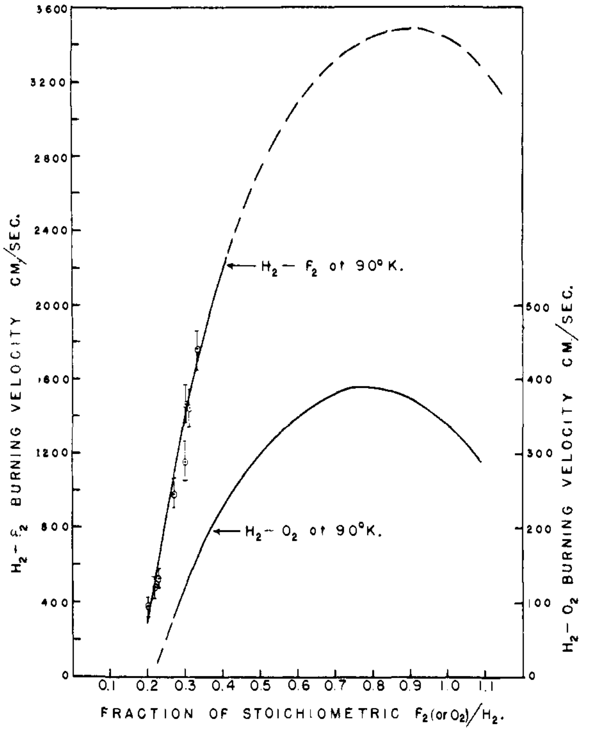

Fig. 1.—Burning velocities of H_2–F_2 and H_2–O_2 flames at 90°K.

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.