We wish to call attention to the fact that their experimental results are not a contradiction of ours, as the conditions were considerably different, and furthermore their results may be interpreted in a manner consistent with our conclusions.

In the first place if we have a group of normal chlorine atoms formed, approximately 2% of them should in time acquire the energy of activation to the $^2P_1$ state by collisions. These atoms would be capable of forming hydrochloric acid by reaction with hydrogen. If, however, the atoms were destroyed by a reaction such as $ICl + Cl = Cl_2 + I$ before they acquired this energy, there would be no hydrochloric acid formation. Therefore, the most favorable conditions for reaction with hydrogen would be with the hydrogen pressure much higher than the iodine monochloride pressure. Mellor and Iredale had this condition in that they had the hydrogen pressure approximately forty times that of the iodine monochloride, whereas in our experiments of this kind the two pressures were of the same magnitude. Our results were confirmed by Franck and Rabinowitsch,[3] who found no reaction between hydrogen and iodine monochloride when they used an electric spark for excitation.

Mellor and Iredale apparently missed the principal point of our argument, namely, that in a given mixture of iodine monochloride, chlorine and hydrogen, light absorbed by the chlorine started a reaction whereas that absorbed by the iodine monochloride did not. That experimental fact is definite proof that the action of light on chlorine gives a product different from that resulting from iodine monochloride. This point is discussed in detail in our previous paper.

DEPARTMENT OF CHEMISTRY   G. K. ROLLEFSON
UNIVERSITY OF CALIFORNIA   F. E. LINDQUIST
BERKELEY, CALIFORNIA
RECEIVED FEBRUARY 16, 1931
PUBLISHED MARCH 6, 1931

THE REMOVAL OF HYDROGEN HALIDE FROM ORGANIC HALIDES

Sir:

In view of the recent appearance of an article by Semb and McElvain [THIS JOURNAL, **53**, 690 (1931)] on the reaction of organic halides with secondary amines, we should like to state that we have been investigating the reaction of organic halides with tertiary amines with the hope of using this reaction to determine the relative ease of removal of hydrogen halide from various organic halides. From the work of Semb and McElvain it is apparent that the usual course of the reaction of organic halides with secondary amines, and in particular with piperidine, is the formation of tertiary amines and that the removal of hydrogen halide takes place to a considerable extent only from tertiary halides. In our work using

[3] Franck and Rabinowitsch, *Z. Elektrochem.*, **36**, 794 (1930).

tertiary amines, and in particular pyridine, the main reaction other than quaternary salt formation appears to be the removal of halogen acid, although rearrangement of the quaternary salt to alkyl pyridine hydrohalides has not been excluded. We have used direct titration with standard alkali to determine the extent of elimination of hydrogen halide and have followed the rate of this reaction for a number of alkyl halides. We hope to be able to publish our results shortly.

DEPARTMENT OF CHEMISTRY   C. R. NOLLER
STANFORD UNIVERSITY, CALIFORNIA   R. DINSMORE
RECEIVED FEBRUARY 24, 1931
PUBLISHED MARCH 6, 1931

CALCULATIONS ON THE VELOCITY OF SOUND IN NITROGEN TETROXIDE

Sir:

In a recent publication, Kistiakowsky and Richards[1] describe an attempt to determine the velocity of the dissociation of nitrogen tetroxide from measurements of the velocity of sound in the gas at 25° and various pressures. Their experimental curve for the change in velocity with pressure is not in good agreement with that calculated from the equation of Einstein[2] giving the velocity of sound in a dissociating gas at frequencies below the critical frequency. Kistiakowsky and Richards attribute the deviation to the inaccuracy of the dissociation data of Bodenstein[3] used in the calculations.

In a forthcoming publication, we report new data on the dissociation of nitrogen tetroxide; we have substituted these data in the theoretical equation and compared the result with the curves of Kistiakowsky and Richards. Einstein's derivation assumes that the gas in question is a perfect gas; this is obviously not true for nitrogen tetroxide. Since we have the pressure coefficient of the equilibrium constant, which varies at 25° according to the equation

$$K_p = 0.1426 - 0.7588\ C^0_{N_2O_4}$$

where

$$C^0_{N_2O_4} = \frac{\text{weight of } (N_2O_4 + NO_2)}{92.02}$$

we can calculate, for any given pressure, the deviation from the ideal condition. Further, from our extrapolation to zero pressure, we have a new value for the heat of dissociation—13,960 calories per mole at constant volume. In making the calculations, we have accepted the values assumed by Kistiakowsky and Richards for the specific heats of nitrogen tetroxide and nitrogen dioxide.

We have plotted the velocity of sound, $V_{\text{theoretical}}$, as calculated from

[1] Kistiakowsky and Richards, THIS JOURNAL, **52**, 4661 (1930)

[2] Einstein, *Sitzb. Berl. Akad.*, 380 (1920).

[3] Bodenstein, *Z. physik. Chem.*, **100**, 68 (1922).