the second term correspond to the deviations from the first order rate. For example, if a velocity constant for a first order reaction were calculated for $x = 1$, the observed rate would be about 11% high when $x = 0$.

Since 11% is not more than the experimental error in Kistiakowsky and Smith's velocity constants, it seems that all of their results, with the exception of the two runs at 1440 mm., are consistent with the hypothesis of a bimolecular mechanism for the isomerization. Probably the simplest way to test this hypothesis would be to investigate the effects of inert gases but negative results would be inconclusive because collisions of butene with inert molecules would not necessarily have the same effect as collisions with molecules of their own kind.

It is believed that the assumption of a bimolecular mechanism eliminates some of the difficulties involved in explaining the low energy of activation and in postulating a chain mechanism of unknown nature.

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THE N-ALKYL GROUP OF ACONINE (ACONITINE)

Sir:

Since the first applications of the Herzig-Meyer method for N-alkyl determinations to aconine [H. Schulze, *Arch. Pharm.*, **244,** 165 (1906)], it has been commonly assumed that aconitine (aconine) possesses an N-methyl group. This has apparently not been questioned in the interpretations given by a number of workers to the results obtained in alkyl determinations on aconitine, aconine, etc. [among others, R. Majima and S. Morio, *Ann.*, **476,** 194 (1929); A. Lawson, *J. Chem. Soc.*, 80 (1936); although Henry and Sharp, *J. Chem. Soc.*, 581 (1931) considered the possibility of the presence of an N-ethyl group but rejected it as unprecedented].

In the course of work which is now in progress in this Laboratory on the structure of the aconite alkaloids, we have found that when aconine hydrochloride is fused with potassium hydroxide in an atmosphere of hydrogen, the principal volatile amine formed is ethylamine, which was readily identified as the *picrate*, m. p. 166° [*Anal.* Calcd. for $C_8H_{10}O_7N_4$: C, 35.02; H, 3.59. Found: C, 35.43; H, 3.46], and as the *ethyl phenyl thiourea*, m. p. 100–100.5° [*Anal.* Calcd. for $C_9H_{12}N_2S$: C, 59.93; H, 6.72. Found: C, 59.93; H, 6.58]. Since this result appeared to contradict the long-standing statement of Ehrenberg and Purfürst [*J. prakt. Chem.* [2], **45,** 604 (1892)] that dimethylamine results on fusion of aconine with barium hydroxide, we have also repeated this experiment. Here again only ethylamine could be identified as before. The so-called dimethylamine derivative of Ehrenberg and Purfürst was unquestionably a double platinum salt of ethylamine. These results therefore strongly indicate the presence of an N-ethyl group in aconine and its parent alkaloid, aconitine.

This conclusion was confirmed by a study of the products of the decomposition of aconine hydrochloride with hydriodic acid under the conditions of the usual alkyl determination. After removal of the methyl iodide which comes from the methoxyl groups, the succeeding iodide originating from the N-alkyl group was shown to be ethyl iodide by identification as *ethyl trimethyl ammonium iodide* [R. Willstätter and M. Utzinger, *Ann.*, **382,** 148 (1911)]. *Anal.* Calcd. for $C_5H_{14}NI$: C, 27.91; H, 6.56; I, 59.02. Found: C, 28.42; H, 6.49; I, 58.48. It is not likely that the ethyl iodide could have had another origin, *e. g.*, in a larger grouping to which the cyclic N atom is attached.

Further, in the similar study of oxonitine, which different workers have examined for N-methyl with unconvincing indications, our own determinations have been negative. It is to be concluded that in the transformation of aconitine into oxonitine by oxidation the reaction involves in some way the N-ethyl group which is thus removed. Possibly the acetaldehyde which has been previously reported as a by-product of the reaction may have its origin in this group. Oxonitine may be of betaine or lactam character.

Finally, in the preparation of oxonitine a second, possibly isomeric substance of m. p. 261°, with decomposition, and $[\alpha]^{26}_D$ $-98°$ in chloroform has been isolated as a by-product. *Anal.* Found: C, 61.40, 61.45; H, 6.69, 6.75; N, 2.57, 2.42; OCH_3, 19.18, 19.07; $N(CH_3)$, trace.

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