two recrystallizations from absolute ethyl alcohol and alcohol-ether, melted at 220–22° (uncorr.). It had a specific rotation in alcohol of $[\alpha]^{20}\text{D}$ $-36.25°$ ($\alpha = -0.98°$, $c = 3.4$). The analysis revealed the formula $C_{10}H_{15}ON{\cdot}HCl$. A mixed melting point with ephedrine hydrochloride (Merck) gave no depression. *Anal.* Calcd. for $C_{10}H_{15}ON{\cdot}HCl$: C, 59.56; H, 7.94; N, 6.96; Cl, 17.59. Found: C, 59.81; H, 7.58; N, 7.52; Cl, 17.39.

The possibility that *l*-ephedrine as such is an alkaloid of aconitum napellus appears impossible as the free base, being water soluble, would remain in the mother liquors on precipitation of the whole alkaloids. In addition we were unable to detect ephedrine in aconitine, amorph., omitting the barium hydroxide distillation.

It appears probable that ephedra bases or indole derivatives are part of the molecular arrangement in aconite alkaloids. Each base, however, has to be degraded individually before final conclusions can be drawn.

We express our appreciation to E. Merck, Darmstadt, Germany, for a supply of the amorphous bases, to Merck and Co., Inc., Rahway, for crystalline aconitine.

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RECEIVED FEBRUARY 8, 1936

THE THERMAL DECOMPOSITION OF ETHYLENE OXIDE AND AN INDUCED ACETALDEHYDE DECOMPOSITION

Sir:

The thermal decomposition of ethylene oxide [Heckert and Mack, THIS JOURNAL, **51**, 2706 (1929)] presents certain features which hitherto have not been satisfactorily explained. It appears that the reaction from 380 to 450° proceeds in two consecutive stages with the intermediate formation of an aldehyde; but that the aldehyde decomposes at a temperature over 100° lower than that for pure aldehydes [Fletcher and Hinshelwood, *Proc. Roy. Soc.* (London), **A141,** 41 (1933); Fletcher, *ibid.*, **A146,** 357 (1934); Thomson and Frewing, *J. Chem. Soc.*, 1443 (1935)]. It was originally suggested that an isomerization of ethylene oxide to acetaldehyde occurs, and that the aldehyde undergoes a unimolecular decomposition in virtue of the energy it possesses when it is formed, *viz.*, the energy of activation (52,000 cal.) and heat of isomerization (23,300 cal.). But it has been pointed out [Kassel, "The Kinetics of Homogeneous Gas Reactions," p. 285] that this hypothesis is untenable as the aldehyde would decompose immeasurably fast, and, furthermore, similar decompositions which result in the intermediate formation of an aldehyde, *e. g.*, methyl alcohol [Fletcher, *Proc. Roy. Soc.* (London), **A147,** 119 (1934)], do not show this behavior.

Now when ethylene oxide is passed through a hot tube it is known [F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," 1935, p. 160] that free radicals are produced in greater quantities and at temperatures considerably lower than they are from the simple aldehydes, ketones and ethers. It is suggested therefore that at 400° one or more reactions, which constitute the first and slow stage of the decomposition, take place with the production of free radicals and aldehydes; and that in the second stage such aldehydes are catalytically decomposed by the free radicals present. We have carried out tests and analyses which indicate that the aldehyde is mainly acetaldehyde, but that smaller quantities of acrolein and formaldehyde are present. The different aldehydes may be formed by alternative reactions of the ethylene oxide or by secondary processes.

As might be expected on the above hypothesis, small quantities of ethylene oxide can induce a decomposition of acetaldehyde below 500°, analogously to azomethane, which is also known to yield free radicals [Allen and Sickman, THIS JOURNAL, **56,** 2031 (1934)]. Thus we find that at 443° acetaldehyde at a pressure of 184 mm. is half decomposed in the presence of its isomer. ethylene oxide, at 17 mm. pressure, in three minutes; in its absence in approximately 350 minutes. This induced acetaldehyde decomposition is proportional to the square root of the ethylene oxide pressure, and to rather less than the first power of the aldehyde pressure; it is retarded by foreign inert gases, *e. g.*, helium (as is the second stage of the ethylene oxide decomposition), but the final pressure increase is not changed.

The presence of free radicals from ethylene oxide also accounts for the induced decompositions of methyl bromide, *n*-butane and isopentane found by Heckert and Mack, as, for instance, *n*-butane is known to be sensitive to methyl radicals [Frey, *Ind. Eng. Chem.*, **26,** 200 (1934)].

Further experiments to elucidate the nature of the first stage of the decomposition, and to investigate reactions induced by ethylene oxide, are in progress.

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RECEIVED NOVEMBER 20, 1935

EXCHANGE REACTIONS OF IODINE BY THE METHOD OF RADIOACTIVE INDICATORS*

Sir:

Using the radioactive isotope of iodine [25 min. half-life, Fermi *et al.*, *Proc. Roy. Soc.* (London), **A146,** 483 (1934)] as an indicator, we have investigated several types of reaction involving exchange between the iodine atoms in different compounds. The radio-iodine is prepared by irradiating a saturated solution of sodium iodate containing a little iodide with the neutrons from beryllium and radon [Amaldi *et al.*, *ibid.*, **A149,** 522 (1935)]. Upon acidifying the solution, iodine is set free and is then separated from the bulk of the solution by extraction with ether. The concentrated sample of radio-iodine thus obtained is mixed with an inactive sample (containing approximately the same number of iodine atoms) of the compound which it is desired to study. After a minute or two the free iodine is separated from the compound, the two samples are prepared in a convenient form, usually as silver iodide, and the activity of each is measured by means of a tube counter.

The results obtained thus far are briefly stated as follows: (1) I_2 and I^-, mixed in aqueous solution to form the I_3^- complex, exchange freely. After separation, the activity is found equally distributed between the two forms of the element. (2) I_2 and IO_3^-, shaken together in 1 N H_2SO_4, do not exchange with appreciable speed. After separation, the IO_3^- (measured as $AgIO_3$) is still inactive. However, when I_2 is mixed with IO_3^- in hot 20 N H_2SO_4 and immediately cooled and separated, 10–15% of the activity is found in the IO_3^-. (3) Active I_2 dissolved in C_2H_5I undergoes no exchange, and AgI precipitated from the C_2H_5I is quite inactive. No exchange was found between these substances even when they were heated together for fifteen minutes at 90°. However, when active NaI and inactive C_2H_5I are dissolved together in alcohol and heated to 100° for five minutes, exchange takes place. (4) I_2 mixed with CHI_3 in ether solution undergoes no exchange. The CHI_3 (measured as such) remains inactive after separation from the active I_2. Also, a negative result was obtained when CHI_3 and NaI were dissolved together in alcohol solution.

The partial exchange found in the case of the iodine–iodate mixture suggests an oxidation–reduction reaction proceeding at a measurable rate. Although no net chemical reaction between these substances is possible, the present experiments show that a kinetic equilibrium actually exists in concentrated acid, and it may be possible to measure the rate of the reaction by means of the radioactive indicator method. It is planned to carry out further experiments along this line, and to investigate the analogous reactions with bromine and chlorine. The experimental details will be reported in a later publication.

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