COMMUNICATIONS TO THE EDITOR

3-FURALDEHYDE (3-FURFURAL)

Sir:

"Furfural" or 2-furaldehyde was first obtained one hundred years ago [Döbereiner, *Ann.*, **3**, 141 (1832)]. Its isomer, 3-furaldehyde or 3-furfural, has now been synthesized by the following sequence of reactions: malic acid ⟶ coumalic acid ⟶ methyl coumalate ⟶ methyl bromocoumalate ⟶ 2,4-furandicarboxylic acid ⟶ 3-furancarboxylic acid ⟶ 3-furoyl chloride ⟶ 3-furaldehyde.

The odor of 3-furaldehyde is more remindful of benzaldehyde than is 2-furaldehyde. Some physical constants are: b. p. 144° (732 mm.); n_D^{20} 1.4945; sp. gr. $^{20}_{20}$ 1.111. The phenylhydrazone melts at 149.5°.

3-Furanaldehyde responds to the usual aldehyde tests but *unlike* 2-furanaldehyde it gives no color test with aniline acetate. We have also noted that 2,4-dimethyl-3-furfural gives no aniline acetate test. The new aldehyde appears to be more highly resistant to auto-oxidation than might have been predicted, and is more stable than its isomer.

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THE VELOCITY OF DISSOCIATION OF NITROGEN TETROXIDE BY THE METHOD OF SOUND WAVES

Sir:

In a communication from this Laboratory [Kistiakowsky and Richards, THIS JOURNAL, **52**, 4661 (1930)] it has been demonstrated that with an experimental accuracy of 0.5%, no change in the velocity of sound in nitrogen tetroxide is detected at 25° with frequencies between 9 and 80 k.c. The lower limit thus set for the velocity of dissociation ($k = 5 \times 10^4$) according to the reasoning of Einstein [*Sitz. Akad.*, 380 (1920)] closely approximates the value ($k =$ about 1×10^5) which is obtained from the kinetic theory of gases as the maximum reasonable upper limit. Brass and Tolman [THIS JOURNAL, **54**, 1003 (1932)] by another method have recently obtained positive evidence of the rate of dissociation, and assign to the velocity constant at 25° an order of magnitude ($k = 2.2$ to 8.4×10^4) which accords with these conclusions.

It is now possible to obtain more specific information concerning this reaction by the acoustical method. Apparatus of special design has permitted the study of the velocity of sound in nitrogen tetroxide between 1.0 and 30° and from 130 to 760 mm. pressure at frequencies between 9 and 93 k.c. At 260 mm. pressure and 30° a further study has been made

between 90 and 500 k.c. In both cases the reproducibility of the measurements has proved to be 0.05%. A wall-correction has been evaluated and applied.

The correspondence between measured velocities at zero frequency and those calculated from Einstein's equations is excellent at 260 mm., and indicates that the assumptions underlying the theoretical reasoning may be applied with confidence to the interpretation of these measurements. Since the absorption coefficient is not found to increase noticeably even at 500 k.c., similar reasoning appears legitimate over the entire frequency range which has been studied. Granting this, a straightforward picture of the kinetics of dissociation emerges. The velocity constant at 25° and 260 mm. is approximately 4.8×10^4, and the activation energy of dissociation approximates closely to the heat of dissociation of nitrogen tetroxide. It may be assumed, therefore, that the velocity of association of nitrogen dioxide has little if any temperature coefficient. The velocity of dissociation decreases with decreasing pressure. These conclusions are independent of unavoidable uncertainties concerning the heat capacities of the dioxide and tetroxide molecules, the exact value of the heat of dissociation, and the exact absolute values of the velocity of sound in nitrogen tetroxide at zero frequency.

Recent evidence that the vibrational specific heat terms in carbon dioxide may become inactive at high frequencies of sound [Kneser, *Ann. Physik*, [V] 11, 777 (1931)] has suggested the possibility that a similar effect may appear in nitrogen tetroxide, and has caused a delay of some months in the publication of the conclusions outlined above. It is hoped that the temperature coefficient of the divergence between high and low frequency velocities of sound will provide a means to differentiate between this effect and that discussed by Einstein. When an experimental distinction between the two has been established, the measurements on nitrogen tetroxide will be submitted in detail for publication.

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THE INVERSION OF CRISTOBALITE

Sir:

Supplementing the foregoing note by Dr. J. W. Greig (p. 2846), I may be permitted to quote from a letter received recently from Dr. K. Endell, one of the observers referred to in my discussion of the inversion of cristobalite. Dr. Endell says (in translation): "It appears to me very improbable that this inversion can be delayed. My early observations are probably not entirely conclusive. In recent years I have tested hundreds