

TABLE I  
 ALKYL ARYL KETONES

4-R	°C.	B.p. Mm.	$n_D^{20}$	$d_{20}$	$V_{10}$	Veloc., m./sec. $V_{20}$	$V_{30}$	Mol. sound veloc. at 30°	Ad. comp., dynes cm. <sup>2</sup> at 30° × 10 <sup>12</sup>
A. 4-R-Acetophenones									
H	100	12	1.5280	1.0193	1537 <sup>p</sup>	1502 <sup>p</sup>	1463 <sup>p</sup>	1338	45.9 <sup>p</sup>
Me <sup>a,b</sup>	70	3	1.5303	0.9966	1532	1495	1457	1526	47.2
Et <sup>a,c</sup>	89	3	1.5252	.9849	1526	1487	1453	1704	48.1
Isoprop <sup>d</sup>	109	3	1.5187	.9705	1503	1467	1429	1883	50.5
<i>t</i> -Bu <sup>e</sup>	112	2	1.5168	.9574	1499	1464	1427	2073	51.3
B. 4-R-Propiophenones									
H	90	3	1.5212	1.0014	..	1493 <sup>p</sup>	1456 <sup>p</sup>	1519	47.1 <sup>p</sup>
Me <sup>f</sup>	100	3	1.5238	0.9831	1525	1486	1450	1706	48.4
Et <sup>a,g</sup>	108	3	1.5199	.9704	1517	1481	1444	1889	49.4
Isoprop <sup>h</sup>	125	3	1.5141	.9560	1498	1460	1424	2074	51.6
<i>t</i> -Bu <sup>i</sup>	162	5	1.5138	.9495	1493	1457	1420	2252	52.2
C. 4-R-Isobutyrophenones									
H <sup>j</sup>	107	3	1.5134	0.9747	1486	1448	1408	1704	51.8
Me <sup>k</sup>	119	4	1.5147	.9605	1484	1448	1410	1894	52.4
Et <sup>l</sup>	122	3	1.5126	.9510	1484	1445	1411	2079	52.8
Isoprop <sup>m</sup>	126	2	1.5079	.9383	1474	1433	1399	2268	54.4
<i>t</i> -Bu <sup>n</sup>	132	2	1.5072	.9361	1470	1432	1395	2439	54.9
D. 4-R-Pivalophenones									
H <sup>o</sup>	71	2	1.5057	.9612	1461	1423	1383	1880	54.4
Me <sup>o</sup>	77	2	1.5066	.9486	1461	1425	1387	2072	54.8

<sup>a</sup> A. Klages and G. Lickroth, *Ber.*, **32**, 1558 (1899). <sup>b</sup> M.p., semicarbazone, 205°. <sup>c</sup> M.p., semicarbazone, 196°. <sup>d</sup> O. Widman, *Ber.*, **21**, 2225 (1888); m.p., semicarbazone, 203°. <sup>e</sup> G. F. Hennion and S. F. deC. McLeese, *THIS JOURNAL*, **64**, 2421 (1942); m.p., semicarbazone, 230°. <sup>f</sup> A. Klages, *Ber.*, **35**, 2252 (1902); m.p., semicarbazone, 188°. <sup>g</sup> M.p., semicarbazone, 151°. <sup>h</sup> *Anal.* Calcd.: C, 81.77; H, 9.15. Found: C, 82.07; H, 9.24; m.p., semicarbazone, 158°. <sup>i</sup> H. A. Bruson and O. Stein, *C. A.*, **29**, 4773 (1935); m.p. semicarbazone, 200°. <sup>j</sup> A. Lapworth and V. Steele, *J. Chem. Soc.*, **99**, 1883 (1911); m.p. semicarbazone, 181°. <sup>k</sup> K. V. Auwers, *Ann.*, **408**, 244 (1915); m.p., semicarbazone, 102°. <sup>l</sup> *Anal.* Calcd.: C, 81.77; H, 9.15. Found: C, 81.89; H, 9.40; m.p., semicarbazone, 105°. <sup>m</sup> *Anal.* Calcd.: C, 82.10; H, 9.47. Found: C, 81.84; H, 9.58; m.p., semicarbazone, 107°. <sup>n</sup> G. F. Hennion and L. A. Auspos, *THIS JOURNAL*, **65**, 1603 (1943); m.p., semicarbazone, 116°. <sup>o</sup> D. E. Pearson, *ibid.*, **72**, 4169 (1950). <sup>p</sup> Previously determined, *cf.* ref. 6.

ing, constant index center cuts were used in the determinations of physical properties listed in Table I.<sup>12</sup> Acetophenone and propiophenone were purchased from Matheson Co. and are included for comparison.

**Measurement of Velocity.**—The ultrasonic velocity of the liquids was measured by use of a variable-path ultrasonic interferometer<sup>13</sup> which employs a piezo-electric quartz crystal driven at 500 kc. per second by a crystal-controlled oscillator. All measurements were made with the interferometer submerged in a constant temperature water-bath.

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(12) The expense of ketone synthesis was borne by a contract from the Office of Naval Research. The rates of oxidation of all but the last two have been reported, *cf.* M. J. Craft, B. F. Landrum, E. C. Suratt and C. T. Lester, *THIS JOURNAL*, **73**, 4462 (1951).

(13) D. R. McMillan, Jr., and R. T. Lagemann, *J. Acoust. Soc. Am.*, **19**, 956 (1947).

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## The Behavior of Anthrone on Some Alumina Columns

By J. H. PINCKARD, A. CHATTERJEE AND L. ZECHMEISTER

When a benzene solution of pure, pale-yellow anthrone is adsorbed from benzene on a suitable alumina-celite column, a colored heterogeneous

zone appears within a few minutes. When, subsequently, this adsorbate is washed with large volumes of benzene, the colored zone is resolved and some of its components migrate slowly downwards while much larger quantities of a colorless and non-fluorescent substance runs through the column. The latter substance is, however, not anthrone but anthraquinone. Under the conditions applied the yield varies between 80–90%. In contrast, a mixture of roughly equal parts of anthrone and anthraquinone is obtained in the washings if an "acid" brand of alumina is applied. A celite column has no effect on anthrone.

### Experimental

One gram of vacuum-sublimed analytically pure anthrone (Calcd. for C<sub>14</sub>H<sub>10</sub>O: C, 86.57; H, 5.19. Found: C, 86.71; H, 5.12; m.p. 154–158°, cor.) which according to spectroscopic tests did not contain any anthraquinone, was dissolved in 100 ml. of benzene and poured, with suction, onto a 24 × 4.2 cm. alumina celite column (4:1). (Activated alumina "Alorco," Grade F, –80 mesh, reground to –200 mesh; Celite No. 545, Johns-Manville.) About a 2 cm. broad, brownish-yellow zone appeared near the top which during the subsequent development by means of 8 liters of benzene was resolved into a narrower, very strongly adsorbed brownish-red zone and a pale yellow substance with greenish fluorescence in ultraviolet light. This substance was present in small amounts only and spread over the rest of the adsorbent; only traces of it reached the chromatographic filtrate.

The main product of the conversion, *i.e.*, anthraquinone, ran through much more easily and could be collected from the filtrate. While passing through the column, it quenched

the moderate fluorescence of the commercial alumina. (An authentic sample of anthraquinone behaved very similarly.) The filtrate was evaporated and the anthraquinone isolated in crystals. Its molecular extinction curve, taken in hexane solution, was identical with that of an authentic sample; m.p. 280–284° (cor.).

*Anal.* Calcd. for  $C_{14}H_8O_2$ : C, 80.76; H, 3.87. Found: C, 80.96; H, 3.97.

The yield was about 83% which could be somewhat increased by a subsequent washing with 1 liter of acetone, which, however, also carried some fluorescent and slightly colored material into the filtrate. In every instance  $\frac{3}{4}$  of the product was present in the first 2-liter benzene fraction.

In another experiment 0.1 g. of anthrone was chromatographed on a  $16.5 \times 1.9$  cm. column made up using an acid brand of alumina, viz., "Aluminiumoxyd sauer," manufactured by M. Woelm in Eschwege, Germany. After the adsorbate was washed with benzene which was followed by acetone and ethanol, a photometric estimate showed the ratio, anthrone:anthraquinone = 1:0.8. Presumably, this incomplete reaction was due to lower conversion rates on the acid column. The recovery was practically complete.

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## The Preparation and Properties of Stannous Fluoride<sup>1</sup>

By WM. H. NEBERGALL, JOSEPH C. MUHLER AND HARRY G. DAY

In connection with investigations of the effectiveness of various fluorine-containing compounds in reducing the acid solubility of dental enamel and the incidence of dental caries in rats, stannous fluoride was found to be most effective.<sup>2</sup> Samples of materials labeled "Stannous Fluoride" obtained from several different chemical supply houses and different samples from the same supply house were found to vary widely in appearance, water solubility, melting point and composition. In addition, the effect in reducing the acid solubility of powdered enamel and the incidence of experimental caries in rats has been found to vary when different samples of such "stannous fluorides" were employed. The work reported herewith was done in order to make available stannous fluoride of known and dependable composition, purity and solubility for further studies of the type mentioned, and for extensive clinical programs involving the topical application of stannous fluoride preparations which are now in progress.

5.460 VW	4.454 W	3.878 W	3.511 VS	3.444 S	3.343 S
3.179 VS	3.114 S	2.741 M	2.587 M	2.517 M	2.438 M
2.346 S	2.299 W	2.213 VW	2.105 M	2.080 S	2.049 S
1.977 S	1.945 S	1.929 S	1.884 M	1.848 S	1.787 VW
1.768 S	1.742 VW	1.700 W	1.686 W	1.622 W	1.612 W
1.594 W	1.572 VW	1.555 W	1.525 M(diffuse)	1.500 M	
1.450 M	1.424 W	1.391 W	1.379 W	1.353 W(diffuse)	
1.325 M	1.310 W	1.296 W	1.282 W	1.267 W	1.242 W

The interaction of stannous oxide and hydrofluoric acid has been investigated as a basis for the preparation of stannous fluoride. Although this

(1) Contribution No. 536 from the Department of Chemistry, Indiana University.

(2) J. C. Muller and G. Van Huysen, *J. Dent. Res.*, **26**, 119 (1947); J. C. Muller, T. M. Boyd and G. Van Huysen, *ibid.*, **29**, 182 (1950); J. C. Muller and H. G. Day, *J. Am. Dent. Assoc.*, **41**, 528 (1950); J. C. Muller and H. G. Day, *J. Nutr.*, **44**, 413 (1951).

reaction was studied almost 100 years ago,<sup>3</sup> significant details and properties have never been reported.

### Experimental

**Stannous Fluoride from Stannous Oxide and Hydrofluoric Acid.**—Stannous oxide, 67.4 g. (0.5 mole), was weighed into a 200-ml. polyethylene beaker and sufficient oxygen-free water (15–20 ml.) was added to thoroughly wet the stannous oxide. With an atmosphere of oxygen-free nitrogen maintained above the stannous oxide, it was heated to 60° on a steam-bath, and 46.0 g. (1.1 moles, a 10% excess) of 48% hydrofluoric acid was slowly added while the reaction mixture was being gently swirled. After about one-half of the stannous oxide had dissolved, the reaction became quite vigorous due to the evolution of heat. The reaction mixture was stirred until all of the stannous oxide had dissolved and then placed in a desiccator to cool under an atmosphere of nitrogen. After two hours, the mother liquor was decanted from the first crop of crystals into another polyethylene beaker. Both the crystals and the mother liquor were placed in desiccators over a 1:1 mixture of calcium chloride and potassium hydroxide for the purpose of drying and obtaining a second crop of crystals, respectively. After two days, further drying of the stannous fluoride was carried out over magnesium perchlorate. After 4 days, the second crop of crystals from the mother liquor was collected and dried in the same manner as the first crop; yield first crop, 69%; second crop, 17%; total, 86%. Both crops were identical in purity and properties.

*Anal.* Calcd. for  $SnF_2$ : Sn, 75.75; F, 24.25. Found: Sn, 75.7, 75.8, 75.8; F, 24.0, 24.5, 24.6.

The above procedure for the preparation of stannous fluoride represents the combination of the optimum conditions as ascertained by a study of the following: the effect of suspending the stannous oxide in varying quantities of water; the effect of the initial temperature upon the reaction; the effect of the extent of excess of hydrofluoric acid upon the reaction and nature of the product; the effect of protecting the reaction mixture from oxygen of the air; and the effect of various drying procedures on the nature of the product. Frey<sup>3</sup> reported that an excess of hydrofluoric acid acting upon stannous oxide gave rise to the acid fluoride. In the present investigation, no indications of any product other than the normal salt were found when an excess of acid up to and including 200% was employed.

**Properties of Stannous Fluoride.**—Stannous fluoride crystallizes as colorless prisms and melts at 210–215°. The compound dissolves in water (29.6% at 18°) to form essentially clear solutions initially. After about an hour, aqueous solutions of stannous fluoride become cloudy due to hydrolysis and finally a fine white precipitate, probably stannous hydroxide, begins to separate. The pH of a freshly prepared 2% solution was found to be 2.90, and after standing for 25 hours, the pH was 2.38. The precipitate which forms from hydrolysis was found to contain less than 0.01% fluorine. Clear solutions of stannous fluoride may be maintained by adding a dilute mineral acid to repress the hydrolysis.

**X-Ray Powder Diffraction Data<sup>4</sup> for Stannous Fluoride.**—In the following table are listed the interplanar spacings

("d") and the relative line intensities found to be characteristic  $SnF_2$ :

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(3) E. Frey, *Ann. Chim. Phys.*, [3] **47**, 37 (1856).

(4) Obtained from Metal and Thermit Corporation, Carteret, N. J.

(5) X-Ray diffraction data by A. Lessor, Department of Chemistry, Indiana University.