TABLE I

Compound ortho-formate	Yield, %	Empirical formula	B.p. °C.	B.p. Mm.	d^{20}_4	$n^{20}D$	MR Calcd.	MR Found	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
n-Propyl	95.3	$C_{10}H_{22}O_3$	96–97	20	0.8830	1.4078	53.51	53.21				
n-Butyl	86.3	$C_{13}H_{28}O_3$	141	25	.8682	1.4184	67.18	67.34				
Isobutyl	86.0	$C_{13}H_{28}O_3$	118–120	22	.8584	1.4122	67.18	67.23				
s-Butyl[b]	87.5	$C_{13}H_{28}O_3$	115	23	.8632	1.4141	67.18	67.27	69.19	96.05	12.14	12.27
n-Amyl[b]	74.0	$C_{16}H_{34}O_3$	101–103	0.3	.8714	1.4290	81.02	81.17	70.03	69.99	12.48	12.23
Isoamyl	88.2	$C_{16}H_{34}O_3$	81–83	0.3	.8632	1.4251	81.02	81.14				
n-Hexyl[b]	77.4	$C_{19}H_{40}O_3$	127–128	0.35	.8621	1.4344	94.90	95.66	72.07	71.99	12.74	12.75
Benzyl[b]	[a]	$C_{22}H_{22}O_3$	.....	...	....	1.5645			79.01	78.93	6.63	6.84

[a] Yield was not calculated because attempted distillation decomposed some of the product obtained. [b] New compound.

that several high boiling orthoformates (*l*-menthyl,[11] bornyl[11] and *s*-octyl[12]) have been prepared in this manner.

The modified method of Mkitaryan and Hunter was applied to the preparation of seven orthoformates with yields ranging from 74 to 95%. Experiments were also carried out for the preparation of isopropyl and *t*-butyl orthoformates but in each case the interchange did not occur. The preparation of allyl orthoformate led to a mixture of products that could not be separated by distillation. Benzyl and *n*-octyl orthoformates decomposed on distillation at 0.3 mm. pressure, but the benzyl orthoformate was found to crystallize in cold storage (4 to 10°), m.p. about 8°.

Experimental[13]

In all cases the ethyl orthoformate and the alcohols employed were distilled to constant refractive index before use.

The experiments summarized in Table I were carried out according to the following procedure. It is illustrated here with the preparation of *s*-butyl orthoformate.

***s*-Butyl Orthoformate.**—To a 500-ml. flask was added 74.1 g. (0.5 mole) of ethyl orthoformate and 128.2 g. (2.0 moles) of *s*-butyl alcohol. A "Thermocap" was used and adjusted so that a maximum temperature of the condensing vapor was 79° by controlling the heat to the flask. The mixture was heated for 24 hours (removing the ethyl alcohol as it was formed) and the vapor rectified through a fourteen inch column packed with glass helices. Upon removal of the theoretical amount of ethyl alcohol (69.0 g., 1.5 moles), the mixture was distilled under vacuum. *s*-Butyl orthoformate was obtained as a colorless liquid (see Table I).

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(11) V. G. Mkitaryan, *J. Gen. Chem.* (*U. S. S. R.*), **8**, 1361 (1938); *C. A.*, **33**, 4222 (1939).

(12) H. Hunter, *J. Chem. Soc.*, **125**, 1389 (1924).

(13) All boiling points are uncorrected.

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Reactions of Nitrous Acid

BY A. T. AUSTIN, E. D. HUGHES, C. K. INGOLD AND J. H. RIDD

It was shown by T. W. J. Taylor, for the aqueous deamination of primary aliphatic amines by nitrous acid,[1] that the reaction rate has the form

$$\text{Rate } \alpha \text{ [amine][HNO}_2]^2$$

where [amine] means the concentration of free amine, and $[HNO_2]$ that of undissociated acid, this specification taking adequate care of the dependence of the rate on *p*H; the equation can be put into other forms, because kinetics cannot locate rapidly transferable protons. Taylor observed the same kinetic law for the formation of nitrosamines from aliphatic secondary amines.[2] Abel and his co-workers obtained it again for the reaction of ammonia with nitrous acid.[3] Schmid and Muhr obtained it yet again for the diazotization of aromatic primary amines.[4] The implication is that it is a kinetic law for rate-controlling N-nitrosation.

Of the various interpretations which have been suggested, that of Hammett[5] has been proved to be correct.[6] It is simply that the active nitrosating agent in mildly acidic aqueous conditions is dinitrogen trioxide.

Papers by Dusenbury and Powell have just appeared[7] in which the opinion is expressed that Taylor's rate law is erroneous, and, in particular, that the second ("unnecessary") molecule of nitrous acid which it involves is "non-existent." They do not state that they have repeated Taylor's work. Now it happens that we have repeated nearly the whole of it, and we therefore feel it encumbent on us to report that we have found it to be entirely accurate.

For ammonia and methylamine Dusenbury and Powell observed the rate law

$$\text{Rate} \propto \text{[amine][HNO}_2][H^+]$$

But they were working in phosphate buffers; they could have been replacing the usual nitrosating agent, dinitrogen trioxide, by a nitrosyl phosphate, or even in part by nitrosyl chloride when sodium chloride was added to make up the ionic strength. Any such nitrosyl compound of an anion present in excess, if acting as the deaminating agent, could lead to the observed rate law, as also could the nitrous acidium ion, or the nitrosonium ion. The observed law, without other information, does not diagnose mechanism. Schmidt and Muhr's work indicated the presence of a reaction of amines with nitrosyl chloride. We may mention that we have shown that nitrosyl bromide, and also the nitrous acidium ion, can replace the usual dinitrogen trioxide as nitrosating agent in buffer solutions not very dissimilar to those of Dusen-

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(1) T. W. J. Taylor, *J. Chem. Soc.*, 1099, 1897 (1928).

(2) T. W. J. Taylor and L. S. Price, *ibid.*, 2052 (1929).

(3) E. Abel, H. Schmid and J. Schafranik, *Z. physik. Chem.*, Bodenstein Festband, 510 (1931).

(4) H. Schmid and G. Muhr, *Ber.*, **70**, 421 (1937).

(5) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 294.

(6) E. D. Hughes, C. K. Ingold and J. H. Ridd, *Nature*, **166**, 642 (1950); A. T. Austin, E. D. Hughes, and C. K. Ingold, forthcoming paper.

(7) J. H. Dusenbury and R. E. Powell, THIS JOURNAL, **73**, 3266, 3269 (1951).

bury and Powell. For these reasons we do not doubt either the results of T. W. J. Taylor, or those of Dusenbury and Powell.

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W.C.1, LONDON, ENGLAND RECEIVED SEPTEMBER 18, 1951

Chemistry of Technetium. I. Preparation of Technetium Heptoxide

BY G. E. BOYD, J. W. COBBLE, C. M. NELSON AND W. T. SMITH, JR.[1]

In the study of the chemistry of technetium it was necessary to establish the formula of the compound formed on heating the element in dry oxygen at 400–600°. Fried and co-workers[2] have suggested the product of this reaction may be TcO_3. However, elemental rhenium, when burned under these conditions gives Re_2O_7.[3] We were first led to the view that the oxidation product in reality was Tc_2O_7 by the observation that the titer of a standardized Ce(IV) solution was not changed upon adding milligram quantities of the compound. Furthermore, the absorption spectrum (Fig. 1) of an aqueous solution of the oxide was found to be identical before and after its treatment with alkaline H_2O_2 suggesting that the technetium was already Tc(VII).

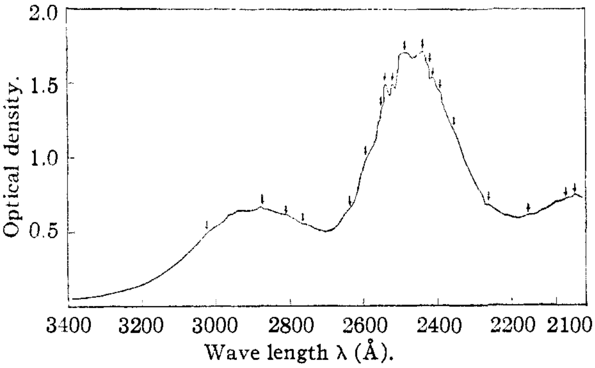

Fig. 1.—Ultraviolet absorption spectra of 3×10^{-4} *M* NH_4TcO_4 *vs.* H_2O at 25° determined with Beckman model DU spectrophotometer using variable slit width and constant sensitivity; source: H_2 discharge lamp. Molar extinction coefficient at 2470 Å. = 4000.

Quantities of technetium metal[4] were burned and the light yellow crystalline oxide (m.p. 119.5 ± 0.1°) formed was purified by repeated sublimations into cooler portions of the quartz reaction tube. An aqueous solution containing a known quantity of the compound was prepared by sealing off an aliquot in a small quartz tube, weighing and breaking the same, and then reweighing its parts after the oxide had dissolved completely. The oxide, which is very hygroscopic, dissolved to give a pink solution whose color disappeared with dilution. A potentiometric *p*H titration was performed using 0.05 *f* ammonium hydroxide. The titration curve, which was characteristic of a strong monobasic acid, showed but one inflection point. The entire neutralized solution was taken to dryness in a platinum dish at 95° and the weight of technetium salt was determined. Pure NH_4TcO_4 is nonhygroscopic and shows no decomposition when kept in air at 100° for several hours. Analytical results from two experiments are given in Table I where a comparison with the titers for Tc_2O_7 and TcO_3, respectively, is made.

TABLE I

EVIDENCE THAT THE FORMULA OF THE YELLOW OXIDE OF TECHNETIUM IS Tc_2O_7

Wt. of oxide, mg.	Millimoles[a] as Tc_2O_7	M.e. as Tc_2O_7	Millimoles as TcO_3	M.e. as TcO_4	M.e. OH^- required	M.e. NH_4TcO_4 found
157.7	0.5087	1.017	1.073	2.146	1.019	1.020
70.11	0.2262	0.4524	0.4769	0.9538	0.4561	0.4564

[a] The theoretical isotopic weight of 99.0 given by Metropolis and Reitinuiner (NP-1980, USAEC, March, 1950) was used in the calculations. Although fission product Tc^{99} may contain small quantities of other isotopes, the amounts will be such as to give a negligible error.

It was concluded that the correct formula for the light yellow oxide produced by heating technetium metal in dry oxygen at 400–600° is Tc_2O_7.

The intense ultraviolet absorption (Fig. 1) of pertechnetate ion in aqueous solutions may be employed for the spectrophotometric determination of Tc(VII). Beer's law was found to hold rather well up to concentrations of 10^{-3} *M* for wave lengths near both maxima (*i.e.*, 2470 and 2890 Å.). As little as 10^{-8} g. of technetium may be detected, which sensitivity compares quite favorably with that obtained spectrochemically.[5] A third absorption band in the far ultraviolet in addition to those previously measured[2] at longer wave lengths is suggested (Fig. 1).

Previously,[6] relatively concentrated strongly acid technetium solutions had been found to show a pink coloration. In this work when a 1 *M* aqueous solution of Tc_2O_7 was slowly evaporated at room temperature over concentrated sulfuric acid, it became yellow, dark yellow, red and dark red; finally, long red-black crystals formed. These hygroscopic crystals were rapidly weighed (15 seconds) and then were allowed to absorb water from the atmosphere to form a dark red solution.

TABLE II

FORMULA OF RED-BLACK CRYSTALS RESULTING FROM THE ISOTHERMAL EVAPORATION OF AQUEOUS Tc_2O_7 SOLUTIONS

Tc_2O_7 hydrate, mg.	Weight of NH_4TcO_4 formed, mg.	Mol. wt. of hydrate	Hydrate formula
1st weighing, 98.1	108.5	327.4	$Tc_2O_7(H_2O)_{0.97}$
2nd weighing, 98.5	. . .	328.6	$Tc_2O_7(H_2O)_{1.03}$

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(1) Department of Chemistry, University of Tennessee, Knoxville, Tenn.

(2) S. Fried, A. H. Jaffey, N. F. Hall and L. E. Glendenin, *Phys. Rev.*, **81**, 741 (1951).

(3) A. D. Melaven, J. N. Fowle, W. Brickell and C. F. Hiskey, "Inorganic Syntheses," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 188.

(4) The pure metal was produced from technetium separated from a "crude" tetraphenylarsonium perchlorate + pertechnetate precipitate dissolved in concentrated H_2SO_4 kindly supplied to us by G. W. Parker, leader of the "hot" laboratory group, Chemistry Division, ORNL. The details of the preparation will be reported in another communication.

(5) D. Timma, *J. Optical Soc.*, **39**, 898 (1949).

(6) E. E. Motta, G. E. Boyd and Q. V. Larson, *Phys. Rev.*, **72**, 1270 (1947).