tert-Butyl Cation Formation in the Hydrolysis of 2-Methyl-2-propanesulfonyl Chloride, the Simplest Tertiary Alkanesulfonyl Chloride[1]

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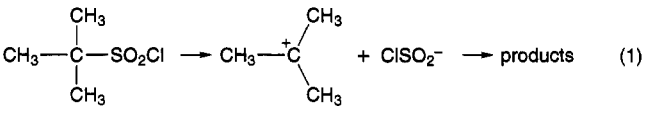
Evidence is presented that the only significant reaction of 2-methyl-2-propanesulfonyl chloride (**1**) (a) in water over the pH range 3.5–13.0 or (b) in methanol–chloroform-*d* is an ionization to the *tert*-butyl cation (**2**) and the chlorosulfite anion ($ClSO_2^-$), followed by further reactions of these species. The organic products include isobutylene (**3**), *tert*-butyl chloride (**4a**), *tert*-butyl alcohol (**4b**), and, at high pH, 2-methyl-2-propanesulfinate anion (**6**) and small amounts of 2-methyl-2-propanesulfonate anion (**5**). In the presence of barium chloride the rate of hydrolysis of **1** is constant over the pH range 3.5–12.0.

The general outline of the mechanisms of hydrolysis of most sulfonyl chlorides in the pH range 3–11 is reasonably well understood.[3] The rate law is commonly of the form $k_{OH} = k_w + k_{OH}[OH^-]$, with pH_i, the pH at which $k_w = k_{OH}[OH^-]$, ranging around 7.1 ± 1.3 for alkanesulfonyl chlorides[4] and 9.5 ± 0.9 for arenesulfonyl[5] and alkenesulfonyl[6] chlorides. With all of these substrates the low pH reaction (k_w term) is evidently a direct attack of water on the sulfonyl sulfur[7] (assisted by another molecule of water acting as a general base[8]). The nature of the hydroxide reaction, however, differs between the arene- and alkenesulfonyl chlorides on the one hand and alkanesulfonyl chlorides on the other. With the former, hydroxide attacks at the sulfur in an S_N2–S process,[3,5,6] whereas with alkanesulfonyl chlorides bearing an α hydrogen atom the reaction of hydroxide is an elimination to form the sulfene[9] ($RR'C{=}SO_2$), which is subsequently trapped by water (if the pH is somewhere below pH ~11) or hydroxide anion (at higher pH's) to give the sulfonate anion.[4]

An obvious simple question is, what is the mode of reaction of a compound like 2-methyl-2-propanesulfonyl chloride (**1**) ("*tert*-butylsulfonyl chloride"), an alkanesulfonyl chloride lacking an α hydrogen? We present evidence herein that the hydrolysis of **1** in the pH range 3.5–13 involves a rate-determining initial ionization as in eq 1 to the *tert*-butyl cation and (probably) the chlorosulfite anion. The array of observed products arises from reactions of these species (or their further transformation products) with water or each other or with unreacted **1**.



(1)

Previous reports[10,11] on the reactions of **1** gave reason to expect unorthodox behavior in general and difficulties in effecting a displacement at sulfur, in particular. The earliest published descriptions of **1**, plus earlier unpublished information gleaned from indirect sources,[12] indicated that **1** and 2-methyl-2-butanesulfonyl chloride decompose readily on warming to give the alkyl chloride, the alkene, sulfur dioxide, and hydrogen chloride, as in eq 2; the reported[10] rate constants for thermal decompo-

$$\underset{\mathbf{1}}{} \xrightarrow{\Delta} \underset{\mathbf{3}}{Me_2C{=}CH_2} + \underset{\mathbf{4a}}{Me_3CCl} + SO_2 + HCl \qquad (2)$$

sition of **1** corresponded to $t_{1/2}$ values of 33 and 1.65 h at 35 and 65 °C, respectively.

Attempts to prepare conventional derivatives met with only limited success. The phenylhydrazide ($Me_3CSO_2NHNHPh$) was obtained[11] in unspecified yield on reaction of **1** with phenylhydrazine, but reaction with cyclohexylamine, morpholine, aniline,[11] or dimethylamine,[13] or of methanol and bases,[11,13] gave no amide or ester. Scott and co-workers,[10] in fact, reported that **1** with cyclohexylamine or benzylamine gave only *tert*-butyl chloride (**4a**) and the sulfur dioxide complex of the amine. The failure to obtain amides and esters from **1** cannot be assigned to any unusual instability of these compounds, since they are readily obtained by other routes.[14] Asinger and coworkers[11] reported that attempts to make the sulfonic acid by treatment with water alone or with dilute sodium hydroxide were unsuccessful but that reaction with 10%

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(1) Organic Sulfur Mechanisms. 38. Part 37: see ref 2.

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(9) Review: King, J. F.; Rathore, R. In *The Chemistry of Sulphonic Acids, Esters, and Their Derivatives*; Patai, S., Rappoport, Z., Eds:, John Wiley and Sons: Chichester, England, 1991; Chapter 17, pp 697–766.

(10) van Aller, R. T.; Scott, R. B., Jr.; Brockelbank, E. L. *J. Org. Chem.* **1966**, *31*, 2357–2365.

(11) Asinger, F.; Laue, P.; Fell, B.; Gubelt, G. *Chem. Ber.* **1967**, *100*, 1696–1700.

(12) Hunt, M. Cited by Nersasian, A.; Andersen, D. E. *J. Appl. Polymer Sci. IV*, **1960**, 74–80. See also refs 10 and 11.

(13) Kopinke, F. D.; Kröckel, W.; Pritzkow, W.; Mateew, K.; Radeglia, R. *J. Prakt. Chem.* **1979**, *321*, 107–111.

(14) Either by (a) oxidation of the corresponding derivatives of 2-methyl-2-propanesulfinic acid[10,15] or, (b) for the amides, reaction of 2-methyl-2-propanesulfinyl chloride with hydroxylamines.[16]

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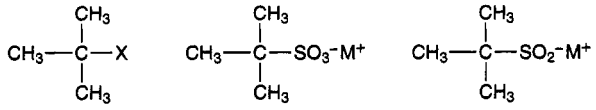
Table 1. Pseudo-First-Order Rate Constants for the Hydrolysis of 2-Methyl-2-propanesulfonyl Chloride (1)

temp (°C)	salt (0.1 M)	pH	k_{obs} (s^{-1})
25	KCl	3.5	1.44×10^{-2}
		4.0	1.49×10^{-2}
		5.0	1.48×10^{-2}
1	KCl	4.0	3.85×10^{-4}
		5.0	3.70×10^{-4}
		6.0	3.50×10^{-4}
1	$BaCl_2$	4.0	3.50×10^{-4}
		8.0	3.50×10^{-4}
		10.0	3.55×10^{-4}
		12.0	3.50×10^{-4}

aqueous NaOH in the presence of pyridine gave (after ion exchange) 2-methyl-2-propanesulfonic acid (**5a**) in 18% yield.

Results and Discussion

Products and Kinetics. The reaction of **1** in D_2O in a closed system (see Experimental Section) gave a product which showed ^1H and ^{13}C NMR signals appropriate to *tert*-butyl alcohol (**4b**), *tert*-butyl chloride (**4a**), and isobutylene (**3**) in the material extracted into $CDCl_3$ and



4
(a) X = Cl
(b) X = OH (or OD)
(c) X = N_3
(d) X = OCH_3

5
(a) M = H_3O
(b) M = Na
(c) M = Ba/2

6
(a) M = Na
(b) M = Ba/2

only **4b** in the D_2O phase. In the presence of sodium azide (2 M), **1** in H_2O gave, in addition to **3**, **4a**, and **4b**, *tert*-butyl azide (**4c**) (ratio of **3**, **4a**, **4b**, **4c**: 6:3:34:57) in the $CDCl_3$ extract. With **1** and NaOD (1 M) in D_2O the $CDCl_3$ extract showed **4a** and **4b**, and in the D_2O phase, in addition to **4b**, also sodium 2-methyl-2-propanesulfinate (**6a**) and a little 2-methyl-2-propanesulfonate (**5b**) (ratio 18:1).

The rate of hydrolysis of **1** was measured by the pH-stat technique. The observed rate constants at 25 °C (in 0.1 M KCl) showed a constant value 1.47×10^{-2} s^{-1}, in the pH range 3.5–5.0 (see Table 1); higher pH's appeared to lead to an increase in rate not conveniently measured with our apparatus. At 1 °C (in 0.1 M KCl) again k_{obs} was constant at low pH (3.68×10^{-4} s^{-1} from pH 4.0–6.0), but at higher pH reproducible rate constants proved difficult to obtain. The formation of **6a**, noted above, pointed to the possibility of the intervention of sulfite anion, presumably formed at pH ≥8 from sulfur dioxide[17] arising from the $ClSO_2^-$. In spite of the report of Asinger *et al.*[11] that attempted reduction of **1** with sodium sulfite gave a negative result, it seemed highly likely that this was indeed the source of the sulfinate **6a**. In our hands **1** was readily transformed by Na_2SO_3 into **6a**, its structure being confirmed by its conversion with methyl iodide into *tert*-butyl methyl sulfone, Me_3CSO_2Me.

Accordingly, rate measurements (at 1 °C) were carried out in 0.1 M $BaCl_2$ (to precipitate most of the sulfite as $BaSO_3$), and as may be seen from Table 1, the rate of hydrolysis in the presence of Ba^{2+} is constant from pH 4.0–12.0. The products of the reaction of **1** in D_2O under basic conditions (NMR tube) in the presence of sodium and barium cations are in accord with the rate measurements. With NaOD in D_2O at pD 13.4 the solution showed NMR signals due to *tert*-butyl alcohol (**4b**) (68%), the sulfinate **6a** (28%), and a little of the sulfonate **5b** (4%). With saturated barium hydroxide (pD 13.4) under the same conditions the product was almost entirely **4b** (92%) with only small amounts of the sulfinate **6b** (3%) and the sulfonate **5c** (5%).

These observations are consistent with a mechanistic picture in which the simple ionization process shown in eq 1 is the only reaction involving **1** and water (or hydronium or hydroxide ions) over the pH range 3.5–13.0. The major products, e.g., **3** and **4**, are formed from *tert*-butyl cation (**2**); the formation of *tert*-butyl chloride (**4a**) and its known speedy hydrolysis (about twice as fast as that of **1**, see below) require that some of the products (**4b** and probably **3**) be formed from **2** arising from further reaction of **4a**. The sulfinate **6** is evidently produced by reaction of **1** with sulfite dianion.

The one possible hydrolysis product unaccounted for in this scheme is the sulfonate salt **5b** or **5c**, which, in principle, could arise in three ways: (a) S_N2-S attack of hydroxide anion on **1**, (b) trapping of *tert*-butyl cation (**2**) with sulfite or bisulfite ions, and (c) oxidation of **6a**, formed as described above. Path a is clearly unimportant in the pH range 3.5–13.0 since (i) there is no sign of any rate increase due to a $k_{OH}[OH^-]$ term and (ii) the amount of **5c** observed in the product of the reaction with $Ba(OH)_2$ was very small. It could conceivably appear at the very highest hydroxide concentrations, e.g., the 10% aqueous NaOH in the presence of pyridine used by Asinger *et al.*[11] Path b involving reaction of **2** with bisulfite would appear to be excluded by the complete absence of any **5b** in the products of hydrolysis in D_2O (with pH varying from ~7 to ~2), in which the concentration of bisulfite can be expected[17] to be maximal and hence most likely to show such a reaction if it should occur at all. A related alternative possibility is the trapping of **2** with sulfite anion. Since SO_3^{2-} has already been shown to react readily with **1** to form **6**, this path would lead to **5b** only under conditions in which $[SO_3^{2-}]$ is sufficiently low that the ionization to **2** (eq 1) competes with the reaction of **1** and SO_3^{2-} to form **6**, while at the same time $[SO_3^{2-}]$ is sufficiently high and the reaction sufficiently efficient that a significant portion of the **2** is trapped to form **5b**. That such trapping is probably not very significant is indicated by an experiment in which *tert*-butyl chloride (**4a**) was allowed to react with an aqueous solution of Na_2SO_3 (1.1 M). The involatile products of this reaction were a mixture of **5b** (2% yield) and sodium 2-methyl-1-propanesulfonate ($Me_2CHCH_2SO_3^-Na^+$) (5% yield); the latter material is presumably formed by the free radical addition of sodium bisulfite onto isobutylene[18] generated *in situ*. The low yield of **5b** would indicate that **2** may be trapped, but only inefficiently, by 1.1 M aqueous Na_2SO_3 and, hence, only to a very minor extent with lower sulfite concentrations. The final route (path c) to the sulfonate salt is oxidation. This process may occur with atmospheric oxygen, apparently by way of a free radical chain reaction,[19] and may well account for most or even all of the sulfonate salt observed.

(17) For a tabulation of the concentrations of the species present in aqueous solutions of sulfur dioxide at various pH values see: Guthrie, J. P. *Can. J. Chem.* **1979**, *57*, 454–457.

(18) Kharasch, M. S.; May, E. M.; Mayo, F. R. *J. Org. Chem.* **1938**, *3*, 175–192.

The observation that the hydrolysis of **1** is fast (k_w 1.47 × 10^{-2} s^{-1}) is fully consistent only with the mechanism in eq 1 and not with an S_N2–S attack of water. The S_N2–S reactions of water with $MeSO_2Cl$, $EtSO_2Cl$, and *i*-$PrSO_2Cl$ have specific rates[4] at 25 °C of 2.10 × 10^{-4}, 3.21 × 10^{-4}, and 3.70 × 10^{-5} s^{-1}, respectively, and the same reaction of **1** must, for steric reasons, be distinctly slower. Similarly, when one notes that the rate constant ratio (k_{OH}/k_w) for the S_N2–S reactions of water vs hydroxide is typically in the range[5] 10^3–10^5, the failure to observe significant S_N2-S attack by hydroxide on **1** is also not surprising. In short, in comparison with the other alkyl groups, a *tert*-butyl group slows the "normal" S_N2–S reactions of water and hydroxide and at the same time greatly accelerates the ionization as in eq 1.

There is a question about the timing of the cleavage of the S–Cl bond, i.e., whether the initial ionization yields **2** and the chlorosulfite anion which *subsequently* decomposes to SO_2 and Cl^- or whether the reaction takes place with a fragmentation concerted with the ionization. Such ionization–fragmentation pathways have been suggested for the related hydrolysis of a tertiary chloroformate ester.[20] In addition, some years ago we adduced evidence that the formation of benzyl bromide and SO_2 by the action of bromide ion on phenylmethanesulfonyl bromide (with the formal loss of $BrSO_2^-$), probably proceeds by a bimolecular substitution–fragmentation process;[21] for the corresponding (slower) reaction of chloride ion and phenylmethanesulfonyl chloride the S_N2 fragmentation also seemed quite possible. On the other hand recent studies of the chlorosulfite anion[22,23] provide evidence for its existence as a discrete species. In particular, Kuhn *et al.*[23] have determined the structure of the $ClSO_2^-$ anion in crystals formed from a reaction in ether; unless there is a truly remarkable effect of water on the chlorosulfite anion the substitution–fragmentation picture with **1** seems unlikely.

The present results provide a quantitative indicator of the nucleofugality of the chlorosulfonyl group (regardless of whether it leaves as $ClSO_2^-$ or as SO_2 and Cl^-). The rate constants for hydrolysis (at 25 °C) of **1** and *tert*-butyl chloride[24] (**4a**) are, respectively, 1.47 × 10^{-2} and 2.975 × 10^{-2} s^{-1}. If we assume that these numbers reflect the relative rates of ionization, then the chlorosulfonyl group is half as reactive as the chloro function as a leaving group in carbocation formation. Though often obscured by other reactions, transformations in which the chlorosulfonyl group acts as a leaving group have been reported.[25] The only earlier piece of quantitative information is our observation[25a] that the reaction of pyridine with ethane-1,2-disulfonyl chloride ($ClSO_2CH_2CH_2SO_2Cl$) to form (transitory) ethenesulfonyl chloride ($CH_2{=}CHSO_2Cl$) is slightly faster than the analogous formation of the same product from $ClCH_2CH_2SO_2Cl$. It seems that the chloro and chlorosulfonyl functions are of roughly comparable nucleofugality, with minor changes in relative rate depending on the specific reaction.

One factor favoring carbocation formation in the above experiments is the use of water as the solvent. It was therefore of interest to look at the reaction of **1** with methanol in $CDCl_3$, in which the ionization would be expected to be slower than in water. In MeOH–$CDCl_3$ after 3 days NMR signals appropriate to *tert*-butyl chloride and *tert*-butyl methyl ether, but no peaks due to the ester, methyl 2-methyl-2-propanesulfonate, Me_3CSO_2OMe, were observed.

It is evident that in polar media the major and perhaps the only reaction is that shown in eq 1. In nonpolar, aprotic media **1** decomposes unimolecularly to give a mixture of **3**, **4a**, sulfur dioxide, and hydrogen chloride,[10,11] presumably either by way of ionic intermediates as in eq 1 or via a cyclic transition state,[10] probably with substantial separation of charge.

The one clearly different reaction of **1** that has been described is that with phenylhydrazine in refluxing ether, reported by Asinger *et al.*[11] to give the phenylhydrazide, $Me_3CSO_2NHNHPh$; we repeated this reaction and obtained the same product in 16% yield. If this reaction is really a direct displacement at sulfur, it would appear to be the only one as yet found with **1**, suggesting the intervention of a significant α-effect. This is consistent with the report of Oae and Kadoma,[26] who examined the rates of reactions of amines with *p*-toluenesulfonyl chloride in acetonitrile and found with hydrazine a positive deviation from the Brønsted plot corresponding to a 40-fold rate enhancement.

Experimental Section

General procedures have been described elsewhere.[2]

Materials and Authentic Specimens. (a) 2-Methyl-2-propanesulfonyl Chloride (1). A solution of *tert*-butyl chloride (**4a**) (20.0 g, 0.22 mol) in anhydrous ether (500 mL) was added dropwise to Mg powder (Fisher "coarse", 5.2 g, 0.22 mol) with stirring in a 1 L three-neck flask under nitrogen. The reaction started after being stirred for 20 min, and stirring was continued for 4 h to give a dark gray solution of $(CH_3)_3CMgCl$. SO_2 gas was bubbled vigorously into the precooled reaction mixture for 20 min to give a dark green solution and the solvent evaporated to give the magnesium sulfinate. The residue was triturated with warm water (60 °C, 200 mL) and the mixture filtered. Cl_2 gas was bubbled vigorously into the precooled filtrate for 20 min and the white solid product extracted with CH_2Cl_2 (150 mL). The CH_2Cl_2 extract was dried ($MgSO_4$) and evaporated to give **1** (10.8 g, 31% yield) as a white solid: mp 97.5–98.0 °C (lit.[10,11,13] mp 95–95.5, 97, 95 °C); IR ν_{max} 1142, 1352, 2996 cm^{-1}; ^1H NMR δ 1.60 (s) (lit.[13] ^1H NMR δ 1.65); ^{13}C NMR δ 24.6, 74.2, (lit.[13] ^{13}C NMR δ 24.5, 74.2). **(b) 2-Methyl-2-propanesulfonic acid (5a)** was obtained in 75% yield from 2-methyl-2-propanethiol and a mixture of 30% H_2O_2 and glacial acetic acid:[27] mp 115 °C (lit.[27] mp 114–116 °C (monohydrate)); IR ν_{max} 1044, 1125 cm^{-1}; ^1H NMR (D_2O) δ 1.31(s); ^{13}C NMR (D_2O) 27.0, 58.0. **(c) Sodium 2-methyl-2-propanesulfonate (5b, M = Na)** was made by neutralizing an aqueous solution of **5a** with NaOH and evaporating the water: IR ν_{max} 1051, 1192 cm^{-1}; NMR spectra same as **5a**. **(d) Sodium 2-Methyl-1-propanesulfonate.** A mixture of isobutyl chloride (5 g, 54 mmol), sodium sulfite (7 g, 56 mmol), water (50 mL), and DME (40 mL) was refluxed for 20 h. The solvent was evaporated and the residue extracted with ethanol which, on evaporation, yielded a white solid (6.8 g, 79%): ^1H

(19) See, for example: Hoyle, J. In *The Chemistry of Sulphinic Acids, Esters, and Their Derivatives*; Patai, S., Ed:, John Wiley and Sons: Chichester, England, 1990; Chapter 14, pp 453–474, especially 456–457, and references cited therein.

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NMR δ (D_2O) 1.04, (d, 6H), 2.09 (m, 1 H), 2.81 (d, 2H); ^{13}C NMR δ 24.5, 27.6, 61.5. **(e) Methyl 2-Methyl-2-propanesulfonate.** A mixture of trimethyl orthoformate (1.5 mL, 13.7 mmol) and **5a** (170 mg, 1.1 mmol) was heated for 19 h at 60 °C under N_2.[28] The volatile material was then evaporated and the residue distilled onto a cold finger (bath temperature 68 °C, 2.5 Torr) (lit.[29] bp 56 °C, 3 Torr): ^1H NMR δ 1.27 (s, 9H), 3.72 (s, 3H); ^{13}C NMR δ 24.5, 55.2, 59.2; exact mass calcd for $C_5H_{12}O_3S$ (M + 1) 153.0585, found (CI) 153.0580. **(f) *tert*-Butyl Methyl Sulfone.** Oxidation of *tert*-butyl methyl sulfide with 30% H_2O_2 in glacial acetic acid[30] gave the sulfone as colorless crystals (from CCl_4): mp 82–84 °C (lit.[31] mp 82–83 °C); ^1H NMR δ 1.39 (s, 9H), 2.77 (s, 3H); ^{13}C NMR δ 23.3, 34.1, 58.6. **(g) *tert*-Butyl Azide (4c).** **4a** (5.0 g, 54 mmol) was added to a stirred solution of NaN_3 (10.0 g, 50 mmol) in water (50 mL) and stirring continued at rt for 60 h. On fractional distillation the fraction boiling around 50 °C was collected (1.0 g, 18%): IR ν_{max} 2130 cm^{-1}; ^1H NMR δ 1.29 (s); ^{13}C NMR δ 27.8, 59.1, plus a peak at 30.8 ppm due to ~10% of **4b**; exact mass calcd for $C_4H_9N_3$ 99.0796, found 99.0799. **(h) *tert*-Butyl chloride (4a):** δ_H ($CDCl_3$) 1.63, δ_C 34.5, 67.5. **(i) Isobutylene[32] (3):** δ_H ($CDCl_3$) 1.71 (t, J = 1.1 Hz, 6H), 4.65 (sept, 2H) δ_C 24.1, 110.6, 142.4. **(j) *tert*-Butyl alcohol (4b):** δ_H ($CDCl_3$) 1.27, (D_2O) 1.24, (CD_3OD) 1.21, δ_C ($CDCl_3$) 31.2, 69.2, (D_2O) 32.3, 72.4, (CD_3OD) 31.2, 69.4. **(k) Di-*tert*-butyl ether:[33]** δ_H ($CDCl_3$) 1.27, δ_C 31.7, 73.8. **(l) *tert*-Butyl methyl ether (4d):** δ_H ($CDCl_3$) 1.13, 3.15, (CD_3OD) 1.18, 3.25, δ_C ($CDCl_3$) 26.9, 49.4, 72.7, (CD_3OD) 27.2, 49.7, 74.4.

Sodium 2-Methyl-2-propanesulfinate (6a). **1** (100 mg, 0.64 mmol) was added to a stirred solution of Na_2SO_3 (1.5 g, 12 mmol) in D_2O (5 mL) and stirring continued for 1 h. The mixture was concentrated to 1 mL (reduced pressure, rt) and then filtered through glass wool into an NMR tube. The NMR spectra showed signals assigned to **6a** (98%) (δ_H 0.99 (s), δ_C 23.2, 56.9) containing a small amount (2%) of **5b** (δ_H 1.31 (s)). In another experiment **1** (100 mg, 0.64 mmol) was added to a solution of Na_2SO_3 (160 mg, 1.26 mmol) and $NaHCO_3$ (216 mg, 2.6 mmol) in water (3.0 mL) under N_2 at rt. After 45 min the solid had dissolved, and after 2 h the solvent was removed, the residue digested with absolute EtOH, the mixture filtered, and the solvent removed from the filtrate to give **6a** as a white solid (90 mg, 98%) with NMR spectra identical to those given above; addition of 1 drop of **4b** to the solution shifted δ_H from 0.99 to 1.16. A mixture of **6a** (90 mg, 0.62 mmol), methyl iodide (0.5 mL, 2.3 mmol), and methanol (1.0 mL) was refluxed for 22 h. The volatile material was evaporated, the residue taken up in CH_2Cl_2, the solution washed with H_2O and dried, and the solvent evaporated to give a colorless oily solid; one recrystallization from CCl_4 gave *tert*-butyl methyl sulfone (18 mg), mp 82–84 °C, identical (mixed mp, NMR spectra) to the authentic specimen.

***N'*-Phenyl-2-methyl-2-propanesulfonohydrazide.** A solution of **1** (0.54 g, 3.5 mmol) and phenylhydrazine (1.1 g, 10.2 mmol) in THF (50 mL) was refluxed overnight. The reaction mixture was poured into water and extracted with ether, the organic extract washed (aqueous HCl), dried ($MgSO_4$), evaporated, and the product recrystallized (ethanol–water) to give the hydrazide as a pale yellow solid (0.13 g, 16.5% yield): mp 145–146 °C (lit.[11] mp 138 °C); IR ν_{max} 1115, 1300, 3216 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.38 (s, 9H), 5.69 (s, 1H), 5.99 (s, 1H), 6.90 (m, 3H), 7.26 (m, 2H); ^{13}C NMR δ 24.2, 60.1, 110.1, 113.8, 121.3, 129.4; exact mass calcd $C_{10}H_{11}N_2O_2S$ 228.0933, found 228.0933.

Kinetics. The pH-stat apparatus and procedure have been described.[6,34] The initial concentrations of **1** varied from 3.1 × 10^{-4} to 6.2 × 10^{-4} M (added in DME) in 50 mL of 0.1 M aqueous KCl or $BaCl_2$ at 1.0 or 25.0 °C; the reaction was followed by titration with NaOH (0.1 M).

Products of the Hydrolysis of 1. (a) In D_2O. D_2O (10 mL) and **1** (100 mg, 0.64 mmol) were placed in a 50 mL round-bottomed flask into the neck of which was inserted a 75° two-way connecting tube inserted into the neck of a 10 mL round-bottomed flask containing $CDCl_3$ (1.5 mL), and the mixture was stirred for 1 h. The $CDCl_3$ was poured (without opening the system) into the reaction mixture and stirring continued a further 5 min. The $CDCl_3$ layer was removed by Pasteur pipet and passed through a small column of $MgSO_4$ into an NMR tube; ^1H and ^{13}C NMR spectra showed signals due to (a) ($(CH_3)_3COH$ (**4b**) δ_H 1.27 (s); δ_C 31.2, 69.2), (b) ($(CH_3)_3CCl$ (**4a**) δ_H 1.63; δ_C 34.4, 67.8), and (c) ($(CH_3)_2C{=}CH_2$ (**3**) δ_H 1.73 (t, J = 1.1 Hz, 6H), 4.66 (sept, J = 1.1 Hz, 2H); δ_C 24.1, 110.5, 142.5; ratio **4a**:**4b**:**3** = 1:5:1). The volume of the aqueous phase was reduced to 2 mL (at 25 °C); the ^1H NMR spectrum showed mainly **4b** at δ_H 1.24, plus a small signal at 1.31 probably due to a little **5a** (< 5%). **(b) NaOD or $Ba(OH)_2$ in D_2O.** Another experiment differing only in that 1 M NaOD in D_2O replaced the D_2O and that the mixture was stirred for 90 min gave (i) in the $CDCl_3$ extract **4a**, **4b**, and **3** in the ratio 12:69:19 and (ii) in the D_2O layer **4b** (δ_H 1.24), **6a** (δ_H 0.99), and **5a** (δ_H 1.31), ratio 43:54:3. In another experiment **1** (15 mg) was added to 0.01 M NaOH in D_2O (pH meter reading 11.94, pD = meter reading + 0.37 = 12.1, see ref 35) and the reaction at rt followed by NMR. After 20 h the spectra showed signals due to **4b** (δ_H 1.24; δ_C 32.3, 72.4) and **6a** (δ_H 1.16; δ_C 22.9, 56.8) in the ratio 93:7. With more basic NaOH (pD 13.4) the spectra indicated **4b**, **6a**, and **5b** (δ_H 1.29; δ_C 26.9, 58.0) in the ratio 68:28:4; with NaOD in D_2O of pD 13.7, the ratio of **4b**:**6a**:**5b** was 61:32:7. With $Ba(OH)_2$ in D_2O, pD 12.5, in an NMR tube **1** gave a ratio of **4b**:**6b**:**5c** of 96:3:1 and at pD 13.5 (saturated $Ba(OH)_2$) 92:3:5, respectively. **(c) NaN_3 in H_2O.** **1** (0.5 g, 3.2 mmol) in aqueous NaN_3 (30 mL, 2 M) was stirred for 3 h in a flask equipped as above. The $CDCl_3$ layer showed signals due to **4a** (δ_H 1.63 (s)), **4b** (δ_H 1.27 (s), δ_C 31.2), **3** (δ_H 1.73 (t, 6H), 4.67 (m, 2H)), and *t*-BuN_3 (**4c**) (δ_H 1.29 (s), δ_C 28.1, 59.1) in the ratio 6:34:3:57.

***tert*-Butyl Chloride (4a) with Aqueous Sodium Sulfite.** A mixture of **4a** (5 g, 54 mmol), Na_2SO_3 (7 g, 56 mmol), and water (50 mL) was stirred for 48 h and the solvent evaporated. The residue was extracted with ethanol, the solvent evaporated, and the residue (0.65 g, 7% yield) dried at 60 °C for 12 h. The ^1H NMR spectrum (D_2O) showed peaks due to **5b** at δ_H 1.30 (s) and $Me_2CHCH_2SO_3^-$ at δ_H 1.03 (d, 6H), 2.07 (m, 1H), 2.80 (d, 2H), in 2% and 5% yields, respectively.

Reaction of 2-Methyl-2-propanesulfonyl Chloride (1) with Methanol. A mixture of **1** (100 mg, 0.64 mmol) and dry methanol (200 mg, 6.4 mmol) was made up to a total of 0.8 mL with $CDCl_3$ in an NMR tube. After about 3 days the ^1H and ^{13}C NMR spectra showed the absence of **1** and the presence of **4a** (δ_H 1.63, δ_C 34.5, 67.5) and **4d** (δ_H 1.13 (s, (9H), 3.15 (s, 3H), δ_C 26.9, 49.4, 72.7); the identity of the two products was confirmed by (a) GC/mass spectrometry and (b) checking the NMR spectra after addition of authentic samples of **4a** and **4d** to the NMR tube. There was no sign of any methyl 2-methyl-2-propanesulfonate or di-*tert*-butyl ether in the reaction mixture.

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