To make a relatively large quantity of perbromate, several hundred milligrams of XeF_2 was stirred with 4 ml of 0.4 *M* $NaBrO_3$ until the XeF_2 had all reacted. The resulting solution was 0.07 *M* in perbromate. Bromate was removed from this solution by precipitation with excess AgF at 0°. Then the ice-cold supernatant solution was made 0.5 *M* in RbF, and the rubidium perbromate precipitate was isolated, washed with a little ice water, and dissolved to make 5 ml of solution.

Aliquots of this solution were analyzed for bromate by reduction with iodide in 0.1 *M* acid in the presence of molybdate, followed by titration with thiosulfate.[16] Other aliquots were analyzed for perbromate by the HBr method. Still other aliquots were made 6 *M* in HCl and 0.04 *M* in Mo(VI). Excess $SnCl_2$ was added to these aliquots, and they were heated for 30 min in boiling water to reduce the perbromate to bromide. The bromide was then determined by oxidation to BrCN with chlorine in neutral cyanide solution, reduction of the BrCN by acid iodide, and titration with thiosulfate.[17] In this way the solution was found to be $<2 \times 10^{-4}$ *M* in bromate, 0.0302 ± 0.0005 *M* in total bromine, and 0.242 ± 0.001 *N* in total oxidizing power. The ratio of oxidizing power to total bromine agrees well with the value of 8.00 expected for heptavalent bromine, and there can be no doubt that the precipitate contained rubidium perbromate.

A detailed investigation of the properties of perbromates is now being undertaken.

Acknowledgment. The author is grateful to Dr. Martin H. Studier for continued encouragement and many helpful discussions during the course of this investigation. Of particular importance was his persistent suggestion that redoubled effort to synthesize perbromates on a macro scale with tagged bromine might pay off.

---

[16] I. M. Kolthoff, *et al.*, "Volumetric Analysis," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1957, pp 269–270.

[17] E. Schulek, *Anal. Chim. Acta*, **2**, 74 (1948).

Evan H. Appelman
Argonne National Laboratory
Argonne, Illinois 60439
Received February 2, 1968

Perbromic Acid. Mass Spectrum[1]

Sir:

Perbromic acid has been shown to be a stable compound and its mass spectrum has been determined.

Solutions containing alkali perbromates[2] were acidified with dilute sulfuric acid and evaporated on platinum filaments at room temperature. These were placed into the source of a modified[3,4] time-of-flight mass spectrometer (Bendix Corp.) which was then evacuated. When the filaments were heated, mass spectra of $HBrO_4$ were observed. Figure 1 is a photograph of an oscilloscope display of a spectrum showing the parent ion, $HBrO_4^+$, and its principal fragment ions. The ions Br_2^+, Br^+, HBr^+, BrO^+, and $HBrO^+$ were observed also, to a large extent from the independent species, Br_2, HBr, and HBrO. After exhaustion of $HBrO_4$ from the filament, BrO_2 was observed as an independent species. On occasion, Br_2O^+ was observed.

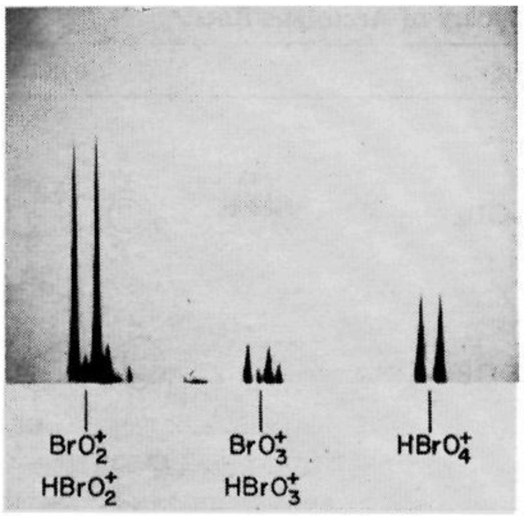


Figure 1. Mass spectrum of perbromic acid (70-V electrons). Each species is represented by two peaks from the nearly equiabundant isotopes Br^{79} and Br^{81}.

For comparison, samples of perchloric acid were run in a similar fashion. The principal ions observed were $HClO_4^+$, ClO_3^+, and ClO_2^+. The relative intensity of $HBrO_3^+$ and $HBrO_2^+$ puts perbromic acid in a position intermediate between periodic acid,[5] from which HIO_3^+ and HIO_2^+ are prominent ions, and perchloric acid, from which $HClO_3^+$ and $HClO_2^+$ are not readily detected.

Perbromic acid seems to be a fairly stable compound. Spectra from a heated sample persisted for an hour. When a filament was cooled, $HBrO_4$ was observed to remain in the source region of the spectrometer for several minutes.

As expected, the volatility of perbromic acid is less than that of perchloric acid. The spectrum of perchloric acid was observed at room temperature as soon as the spectrometer was sufficiently evacuated to operate, whereas the spectrum of perbromic acid was not observed until the filament was heated to about 100°.

---

[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Prepared by E. H. Appelman, *J. Am. Chem. Soc.*, **90**, 1900 (1968).

[3] M. H. Studier, *Rev. Sci. Instr.*, **34**, 1367 (1963).

[4] J. R. Haumann and M. H. Studier, *ibid.*, in press.

[5] M. H. Studier and J. L. Huston, *J. Phys. Chem.*, **71**, 457 (1967).

Martin H. Studier
Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439
Received February 2, 1968

Methoxy Substituent Effects and Anchimeric Assistance in Solvolyses of 2-Benzonorbornenyl Bromobenzenesulfonates[1]

Sir:

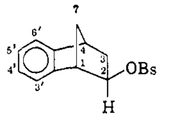
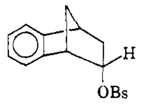
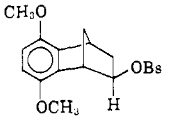
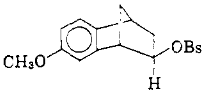
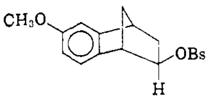
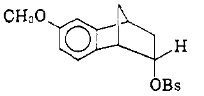
Reactivities and stereochemistry in acetolyses of *exo*- and *endo*-2-benzonorbornenyl bromobenzenesulfonates (*exo*-I-OBs and *endo*-I-OBs) are best interpreted with anchimerically assisted ionization (k_Δ) of the *exo*-I-OBs due to carbon participation and anchimerically unassisted ionization (k_s) of the epimeric *endo*-I-OBs.[2a,b] However, as an indirect criterion for anchimeric assistance due to carbon participation in solvolysis of *exo*-I-

---

[1] Supported in part by the National Science Foundation.

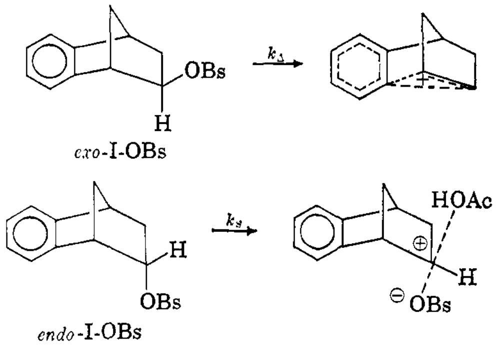
[2] (a) P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960); (b) W. P. Giddings and J. Dirlam, *ibid.*, **85**, 3900 (1963); (c) H. Tanida, K. Tori, and K. Kitahonoki, *ibid.*, **89**, 3212 (1967), ref 27.

Table I. Summary of Acetolysis Rates[a]

Compd	Structure	Temp, °C	10^6k, sec^{-1}	Rel rates
exo-I-OBs		50.0	169[b,d]	
		25.0	6.19	1
endo-I-OBs		100.0	10.2[c,d]	1
		75.0	0.568	
exo-II-OBs		25.0	54.6[e]	8.8
exo-V-OBs		25.0	4.03	0.65
exo-IV-OBs		25.0	930[g]	150
endo-IV-OBs		100.0	25.1[f,g]	2.5
		75.0	1.44	

[a] Anhydrous AcOH with no added NaOAc. [b] $\Delta H^{\ddagger} = 24.7$ kcal/mole; $\Delta S^{\ddagger} = +0.5$ eu. [c] $\Delta H^{\ddagger} = 29.1$ kcal/mole; $\Delta S^{\ddagger} = -3.9$ eu. [d] From these data the *exo*/*endo* rate ratio at 25° is estimated to be 14,800. From the data of Bartlett and Giddings[2a] in AcOH, 0.1 *M* in NaOAc, this ratio is estimated[2a,c] as 15,000. [e] H. Tanida, T. Tsuji, and S. Teratake, *J. Org. Chem.*, **32**, 4121 (1967), have just reported a rate constant approximately twice as large as this in acetic acid containing 0.1 *M* NaOAc. This difference is within the range of salt effects due to the added salt. [f] $\Delta H^{\ddagger} = 28.8$ kcal/mole; $\Delta S^{\ddagger} = -2.7$ eu. [g] From these data the *exo*/*endo* rate ratio at 25° is estimated to be 8.30×10^5.

OBs, Brown and Tritle[3a] have employed *exo*/*endo* solvolysis rate ratios for the series of 2-R-2-benzonorbornenyl systems with R = H, CH_3, and C_6H_5. In a recent communication[3a] they reported similar *exo*/*endo* rate ratios for all three pairs of benzonorbornenyl systems and remarked, "Certainly there is no change in the *exo*/*endo* rate ratio of the magnitude one might have predicted for the major decrease in carbon participation which should have accompanied the introduction of a highly stable tertiary benzylic carbonium center at position 2." They further concluded, "The results are clearly more consistent with the steric explanation than that based on carbon participation. However, we prefer to establish the effect of substituents in the aromatic ring before reaching a final decision."[4,5,5a] In the present communication we report some methoxy substituent effects in acetolysis of 2-benzonorbornenyl bromobenzenesulfonates and their implications as regards carbon participation.



exo-I-OBs

endo-I-OBs

The epimeric parent bromobenzenesulfonates were prepared according to Bartlett and Giddings.[2a] The 3′,6′-dimethoxy derivative, *exo*-II-OBs, mp 71.5–72.0°, was prepared from the corresponding alcohol described previously.[6] Mixtures of 4′- and 5′-methoxy-*exo*-2-benzonorbornenols were prepared from 4′-

---

(3) (a) H. C. Brown and G. L. Tritle, *J. Am. Chem. Soc.*, **88**, 1320 (1966); (b) H. C. Brown, *Chem. Brit.*, 199 (1966); *Chem. Eng. News*, 45, 87 (June 5, 1967).

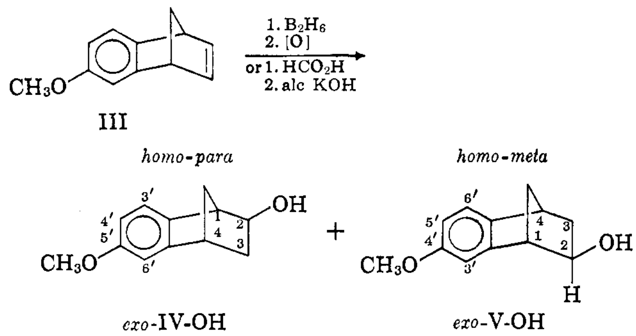
(4) Actually, some information was already available on the effect of 3′,6′-methoxy substitution on the acetolysis rate of *exo*-I-OBs (G. A. Wiley, unpublished results, quoted by A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 389).

(5) Subsequently, at the Fifth Hydrocarbon Symposium, Houston, Texas, April 14, 1966, H. C. Brown reported the solvolytic behavior of a mixture of *homo-p*- and *homo-m*-methoxy-substituted brosylates, *exo*-IV-OBs and *exo*-V-OBs, respectively, prepared from the mixed alcohols resulting from hydroboration–oxidation of the methoxybenzonorbornadiene III. A steady acetolysis rate constant to 90% reaction was observed, the value being somewhat smaller than for the unsubstituted *exo*-I-OBs. On this basis it was concluded that a *homo-p*-methoxy group is not rate enhancing. Actually, on the basis of the present communication, it is clear that either the very reactive *exo*-IV-OBs was destroyed in the work-up or the fast stage of acetolysis due to *exo*-IV-OBs in the mixture was missed.

(5a) Note Added in Proof. We have recently learned through a letter from H. C. Brown to H. Tanida, dated March 4, 1968, that Brown and coworkers have since isolated *exo*-IV-OH by hydrogen chloride addition to III and hydrolysis of the reactive *exo*-IV-Cl. From this letter and one from H. Tanida to S. Winstein dated Feb 24, 1968, we have learned that further work on substituent effects in 2-benzonorbornenyl solvolysis has been done by Tanida and coworkers, as well as Brown and coworkers.

(6) (a) G. A. Wiley, 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 1960, Abstracts, 28-O. (b) Satisfactory carbon and hydrogen analyses were obtained for the new compounds mentioned.

methoxybenzonorbornadiene[7] (III). Hydroboration–oxidation led to a 45:55 mixture, while addition of formic acid at room temperature and subsequent saponification led to a 75:25 mixture of *homo-para* and *homo-meta* alcohols,[8] *exo*-IV-OH and *exo*-V-OH, respectively. Brosylation of the alcohol mixture and careful work-up led to a mixture of very reactive *homo-para* and less-reactive *homo-meta* esters. Acetolysis of this mixture until the more reactive component was consumed and product separation led to the *homo-meta exo*-V-OBs, mp 124–125°, and the *homo-para* acetate. Lithium aluminum hydride reduction of the latter gave the *homo-para exo*-IV-OH, mp 50–51°, which was converted to *exo*-IV-OBs, mp 65° dec. Oxidation of *exo*-IV-OH to the ketone, followed by lithium aluminum hydride reduction, led to the *endo homo-para* alcohol, *endo*-IV-OH, mp 52.5–53.5°, brosylate mp 96–97°. Rates of acetolysis of the bromobenzenesulfonates are summarized in Table I.



Theory and available experience with aryl substituent effects[9] lead one to expect substantial rate enhancement by an *o*- or *p*-methoxyl and slight rate retardation by a *m*-methoxyl group in anchimerically assisted acetolysis involving phenyl participation. On the other hand, such substituent effects should be small for anchimerically unassisted acetolysis. As is clear from Table I, these are just the effects observed, and thus the observed substituent effects are in line with the original interpretation[2a,b] of the acetolysis of the parent I-OBs system involving anchimerically assisted ionization of the *exo* epimer (k_Δ) and anchimerically unassisted ionization of the *endo* (k_s).

The magnitude of the rate-depressing effect of the *homo-m*-methoxy group in the *exo* system (0.65)[10] is quite similar to that of a *m*-methoxy group in acetolysis of neophyl tosylate[9a] (0.74 at 50°). Further, the factor[10] of 150 by which the *homo-p*-methoxy group accelerates the *exo* system is similar in magnitude to those observed for a *p*-MeO group in neophyl,[9a] 3-phenyl-2-butyl,[9b,11] and other esters where anchimerically assisted ionization is already dominant in the unsubstituted case. In contrast with the effect in acetolysis of the *exo* epimer, a *homo-p*-methoxy group in the *endo*-IV-OBs is rate enhancing by a much smaller factor of 2.5.

The factor of 150 corresponds to a ρ of -2.80 in a $\rho\sigma^+$ treatment, comparable to the ρ of -2.96 for neophyl.[9a] This magnitude of ρ also compares favorably with those reported for concerted intermolecular Friedel–Crafts reactions, such as the action of EtBr or *i*-PrBr plus $GaBr_3$ on substituted benzenes (ρ -2.4, -2.3).[12] The similarity in ρ value for *exo*-benzonorbornenyl acetolysis to those for other concerted intramolecular and intermolecular Friedel–Crafts reactions is evidence for the dominance of anchimerically assisted ionization, not only for the *homo-p*-methoxy-substituted *exo* case, but for the unsubstituted *exo* case as well.

The indirect criterion used by Brown and Tritle[3a] is an expected rapid attenuation of the *exo*/*endo* rate ratio as a 2 substituent is added and then made increasingly more electron releasing. This is based on the reasonable supposition that an electron-releasing group will be more rate enhancing for the anchimerically unassisted *endo* derivative than the anchimerically assisted *exo* epimer. However, such substituent effects can be treacherous, since substituents can introduce various steric problems. While it is evident that the indirect criterion fails as a diagnostic probe for anchimerically assisted ionization of *exo*-I-OBs, we are not yet able to analyze quantitatively the various components contributing to the *exo*/*endo* rate ratios. It is still not clear where ionization changes from anchimerically assisted to essentially unassisted as 2-R groups are added. Substituent effects in the tertiary cases would be helpful, and we are investigating these at present.

The same indirect criterion applied to the benzonorbornenyl system by Brown and Tritle[3a] has also been applied[3b] to the norbornyl[13] case. With all the *direct* evidence[13] in line with anchimerically assisted ionization of *exo*-2-norbornyl and anchimerically unassisted ionization of *endo*-2-norbornyl arenesulfonate, it is evident that the *indirect* criterion fails for the parent norbornyl system, just as it does for benzonorbornenyl.

Acknowledgment. We are grateful to Dr. A. Diaz for advice and assistance in connection with several facets of the present work.

---

[7] H. Tanida, R. Muneyuki, and T. Tsuji, *Bull. Chem. Soc. Japan*, 37, 40 (1964).

[8] The signal for the aromatic proton *meta* to the methoxyl appears as two overlapping doublets in the 60-Mc nmr. At 100 Mc two overlapping 1,3,4-trisubstituted benzene patterns appear, one for each isomer. Careful integration gives the ratio of isomers.

[9] (a) S. Winstein and R. Heck, *J. Am. Chem. Soc.*, **78**, 4801 (1956); **79**, 3432 (1957); (b) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, 74, 1113 (1952); S. Winstein, M. Brown, K. Schreiber, and A. H. Schlesinger, *ibid.*, 74, 1140 (1952); S. Winstein and R. Baker, *ibid.*, **86**, 207 (1964), and intervening papers.

[10] These substituent rate factors are for titrimetric rates. They differ from the ionization rate factors to the extent ion-pair return differs in importance for the aryl-substituted and unsubstituted cases being compared. Such differences are small, however, judging by available evidence in other cases.[9b] For *exo*-I-OBs, the polarimetric:titrimetric rate ratio is 4.6 in AcOH at 50° [J. Dirlam, A. Diaz, W. P. Giddings, and S. Winstein, unpublished work).

[11] D. J. Cram, *J. Am. Chem. Soc.*, 71, 3863 (1949); D. J. Cram and J. A. Thompson, *ibid.*, **89**, 6766 (1967), and intervening papers.

[12] L. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 51 (1963).

[13] *E.g.*, (a) S. Winstein and D. S. Trifan, *J. Am. Chem. Soc.*, 71, 2953 (1949); S. Winstein, *ibid.*, **87**, 381 (1965), and intervening papers; (b) E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *ibid.*, **85**, 169 (1963); S. G. Smith and J. P. Petrovitch, *Tetrahedron Letters*, 3363 (1964); (c) B. L. Murr, A. Nickon, T. D. Swartz, and N. H. Werstiuk, *J. Am. Chem. Soc.*, **89**, 1730 (1967); J. M. Jerkunica, S. Borčić, and D. E. Sunko, *ibid.*, **89**, 1732 (1967); (d) E. J. Corey and R. S. Glass, *ibid.*, **89**, 2600 (1967); (e) W. J. le Nobel, B. L. Yates, and A. W. Scaplehorn, *ibid.*, **89**, 3751 (1967); (f) see also P. G. Gassman and J. L. Marshall, *ibid.*, **88**, 2822 (1966); T. G. Traylor and C. L. Perrin, *ibid.*, **88**, 4934 (1966).

[14] National Science Foundation Trainee, 1965–1968.

D. V. Braddon, G. A. Wiley
Department of Chemistry, Syracuse University
Syracuse, New York

J. Dirlam,[14] S. Winstein
Contribution No. 2201, Department of Chemistry
University of California, Los Angeles, California 90024

Received January 1, 1968