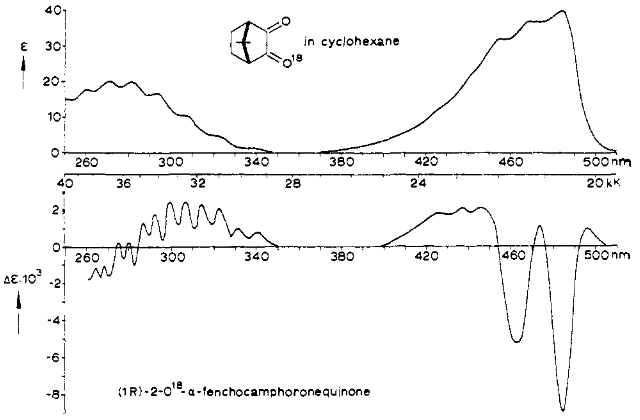


Figure 1.

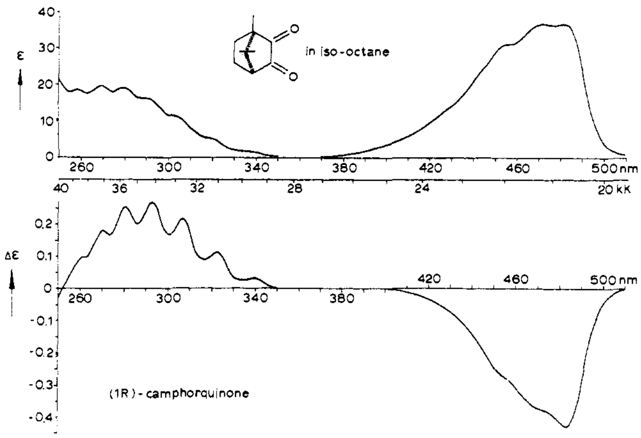


Figure 2.

been measured in any of these compounds, neither in CD nor in ORD. Two ORD curves only show the first half of a Cotton effect.[3]

We have started the synthesis of a number of diketones which derive optical activity from substitution of one ^{16}O by ^{18}O. The first compound which is reported here is an α-diketone: (1*R*)-[2-^{18}O]-α-fenchocamphoronequinone (I). The CD curve between 250 and 520 nm has been measured with a very sensitive instrument built by Mr. Dekkers in this department. Corrected to optical purity it is displayed in Figure 1 together with the absorption curve. Both bands in CD around 280 and 480 nm show exceptionally pronounced structure. For comparison, the CD and absorption spectra of camphorquinone (II) (Figure 2) and of isofenchonequinone (III) (Figure 3) are added.[4]

Recently several papers have been published on the interpretation of electronic spectra and the optical activity of α-diketones.[5,7] The assignment of electronic transitions by some authors[5] differs from the assignment given by others.[7] Nevertheless, they agree in expecting the same sense of twist to be present in the dicarbonyl group of II. However, the opposite sense of twist has been suggested on the basis of conformational analysis.[6]

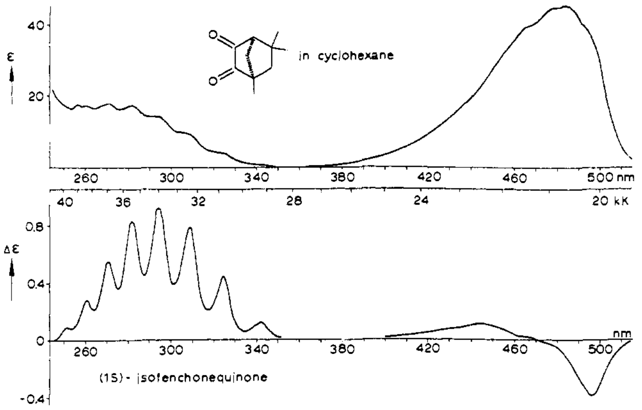


Figure 3.

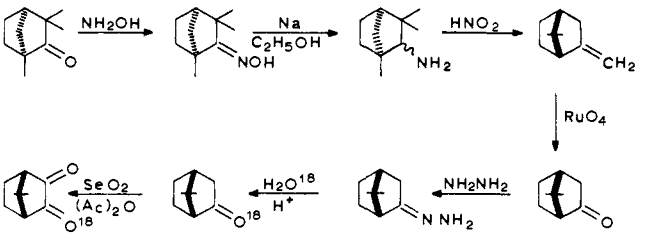


Figure 4. The synthesis of compound I from (+)-(1*S*)-fenchone.

Theoretical analysis of the CD of compound I, which will be published elsewhere, may contribute to clear up these antitheses.

Details of the synthesis of I will be published separately by one of the authors (Kokke). A scheme of the route followed is given in Figure 4.

---

(3) S. Englard, J. S. Britten, and I. Listowsky, *J. Biol. Chem.*, **242**, 2255 (1967); L. Verbit, *J. Amer. Chem. Soc.*, **89**, 167 (1967).

(4) From ORD measurements of III (H.-P. Gervais and A. Rassat, *Bull. Soc. Chim. Fr.*, 745 (1961)) it has been concluded[5,6] that the absorption band around 480 nm gives rise to a normal Cotton effect in CD, which is at variance with our results.

(5) W. Hug and G. Wagnière, *Helv. Chim. Acta*, **54**, 633 (1971); W. Hug, J. Kuhn, K. J. Seibold, H. Labhart, and G. Wagnière, *ibid.*, **54**, 1451 (1971).

(6) A. W. Burgstahler and N. C. Naik, *ibid.*, **54**, 2920 (1971).

(7) E. Charney and L. Tsai, *J. Amer. Chem. Soc.*, **93**, 7123 (1971).

(8) One of the authors (W. C. M. C. Kokke) is indebted to the Netherlands Organization for the Advancement of Pure Research (Z.W.O.) for the sponsoring of this work. A NATO grant for the purchase of ^{18}O is gratefully acknowledged.

W. C. M. C. Kokke,[8] L. J. Oosterhoff*
Gorlaeus Laboratories
Department of Theoretical Organic Chemistry
University of Leiden
Leiden, The Netherlands

Received July 1, 1972

Test of Bond-Order Methods for Predicting the Position of the Minimum-Energy Path for Hydrogen Atom Transfer Reactions

Sir:

The bond-energy–bond-order method (BEBO) of Johnston and Parr can be used to predict a narrow curving parabolic potential energy channel between reactants and products in reactions of the form $A + HB \rightarrow AH + B$.[1,2] The predicted properties of the saddle point have been tested in conjunction with transition state theory and the combination of theories has

---

(1) H. S. Johnston and C. Parr, *J. Amer. Chem. Soc.*, **85**, 2544 (1963).

(2) H. S. Johnston, "Gas Phase Reaction Rate Theory," Ronald Press, New York, N. Y., 1966.

been enormously successful in predicting energies of activation and rate constants.[1-3] (A modified BEBO method and transition state theory have also been applied successfully to more general classes of atom transfer reactions.[4-9])

Recently *ab initio* calculations of high accuracy have been carried out for the position of the minimum-energy path in two such reactions ($A = H$[10] and F[11,12] with $B = H$). This makes possible a test of the BEBO method which tests more than just the saddle point region and which is independent of dynamic assumptions. In particular, since the *ab initio* calculations and BEBO in both cases predict that the minimum-energy path is a collinear one, it is possible to test the use of the Pauling rule relating bond order and bond length for single bonded systems XY[13]

$$R_{XY} = R_e - (0.26\ \text{Å}) \ln n_{XY} \qquad (1)$$

and the concept of conservation of bond orders[14]

$$n_{AH} + n_{HB} = 1 \qquad (2)$$

These two equations suffice for the prediction of the minimum-energy path of any atom transfer reaction involving the making and breaking of a single bond in both the BEBO and modified BEBO methods.[1-9]

One point which must be considered for the comparison is that the minimum-energy path through the (R_{AH}, R_{HB}) plane for collinear collisions is slightly different from the minimum-energy path in other two-dimensional coordinate systems which can be used for collinear collisions.[15] *E.g.*, the insert of Figure 1 compares the former (as determined in ref 10) to the minimum-energy path in the normal coordinates used by Shavitt[10] (as determined in ref 15). This comparison shows that the concept of the minimum-energy path without reference to a specific coordinate system is uncertain by at least 0.04 Å for this system. The BEBO minimum-energy path does not contain a reference to a specific coordinate system but it agrees everywhere with either of these two *ab initio* minimum-energy paths within 0.03 Å.

The BEBO method predicts a saddle point height for $H + H_2$ of 9.9 kcal/mol. The best current estimate of the actual $H + H_2$ saddle point height is 9.5 ± 0.5 kcal/mol.[16]

Bender, *et al.*, determined the $F + H_2$ minimum-energy path in the (R_{FH}, R_{HH}) plane from three different *ab initio* calculations: (a) a one-configuration self-consistent-field wave function,[11] (b) a 214-configuration multiconfiguration wave function,[11] and (c) a more accurate multiconfiguration wave function.[12] The results are compared to the BEBO results in Figure 1. The BEBO path agrees with both paths b and c within 0.03 Å. The BEBO saddle point height is 1.7 kcal/mol. A good estimate of the actual saddle point height is that it is midway between those for Muckerman's semiempirical surfaces no. 2 and 3,[17] or 1.2 ± 0.3 kcal/mol.

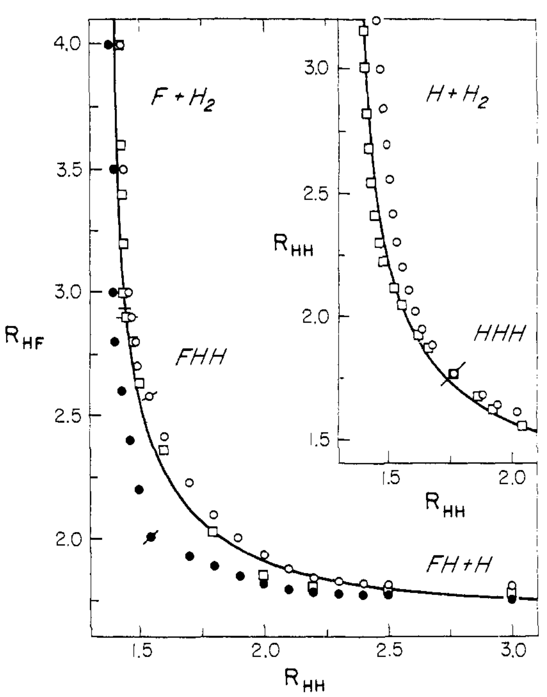


Figure 1. Minimum-energy paths for $H + H_2 \rightarrow H_2 + H$ (insert) and $F + H_2 \rightarrow FH + H$ (large figure) as functions of internuclear distances in bohrs (1 bohr = 0.52917 Å). For $H + H_2$, the circles are on the minimum-energy path in the (R_{HH}, R_{HH}) plane as determined from the *ab initio* potential surface of Shavitt, Stevens, Minn, and Karplus, and the squares are on the minimum-energy path in normal-coordinate space for the same potential energy surface. For $F + H_2$, points on the minimum-energy paths in the (R_{FH}, R_{HH}) plane in calculations (a), (b), and (c) of Bender, O'Neil, Pearson, and Schaefer are given by filled-in circles, open circles, and squares, respectively. For both reactions, the solid line is the bond-energy–bond-order minimum-energy path. In all cases, the position of the saddle point is indicated by a tick mark perpendicular to the minimum-energy path.

Bender, *et al.*, concluded from the good agreement of the minimum-energy paths from calculations b and c that, although method b does not yield an accurate enough exothermicity or saddle point height, it will be useful for evaluating positions of minimum-energy paths. One can estimate that method b required about 5 hr of CDC 6600 computer time to determine the minimum-energy path for $F + H_2$. The BEBO calculations reported here required about 0.05 sec of CDC 6600 computer time for $F + H_2$, or they could be done on a desk calculator.

In summary, the BEBO method contains no adjustable parameters, is very simple and fast, and is very accurate both for the positions of the minimum-energy path and for the barrier heights for the reaction of H and F with H_2.

The saddle point heights $V^{\ddagger}$ predicted by the *ab initio* calculations are in the order $V_a^{\ddagger} > V_b^{\ddagger} > V_c^{\ddagger}$.

(3) S. W. Mayer, L. Schieler, and H. S. Johnston, *J. Chem. Phys.*, **45**, 385 (1966).

(4) Reference 2, p 347.

(5) S. W. Mayer, L. Schieler, and H. S. Johnston in "Eleventh Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1967, p 837.

(6) S. W. Mayer, *J. Phys. Chem.*, **71**, 4159 (1967).

(7) S. W. Mayer and L. Schieler, *ibid.*, **72**, 236 (1968).

(8) S. W. Mayer and L. Schieler, *ibid.*, **72**, 2628 (1968).

(9) S. W. Mayer, *ibid.*, **73**, 3841 (1969).

(10). I. Shavitt, R. M. Stevens, F. L. Minn, and M. Karplus, *J. Chem. Phys.*, **48**, 2700 (1968); see also I. Shavitt, *ibid.*, **49**, 4048 (1968).

(11) C. F. Bender, P. K. Pearson, S. V. O'Neil, and H. F. Schaefer, *ibid.*, **56**, 4626 (1972).

(12) C. F. Bender, S. V. O'Neil, P. K. Pearson, and H. F. Schaefer, *Science*, **176**, 1412 (1972).

(13) L. Pauling, *J. Amer. Chem. Soc.*, **69**, 542 (1947).

(14) H. S. Johnston, *Advan. Chem. Phys.*, **3**, 131 (1960).

(15) D. G. Truhlar and A. Kuppermann, *J. Amer. Chem. Soc.*, **93**, 1840 (1971).

(16) H. F. Schaefer, "The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results," Addison-Wesley, Reading, Mass., 1972, pp 318–319.

(17) J. T. Muckerman, *J. Chem. Phys.*, **56**, 2997 (1972).

It should be noticed the position of the saddle point moves out monotonically toward the $F + H_2$ channel as this height decreases. This should be expected in general for nonthermoneutral reactions[18] and should be a caution against emphasizing[11] a prediction of the geometry of the saddle point when its height is not predicted correctly.

Acknowledgment. This work was supported in part by the National Science Foundation under Grant No. GP-28684. The author is grateful to Professor Fritz Schaefer for discussions.

[18] See, *e.g.*, G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955); M. H. Mok and J. C. Polanyi, *J. Chem. Phys.*, **51**, 1451 (1969); and C. A. Parr and D. G. Truhlar, *J. Phys. Chem.*, **75**, 1844 (1971).

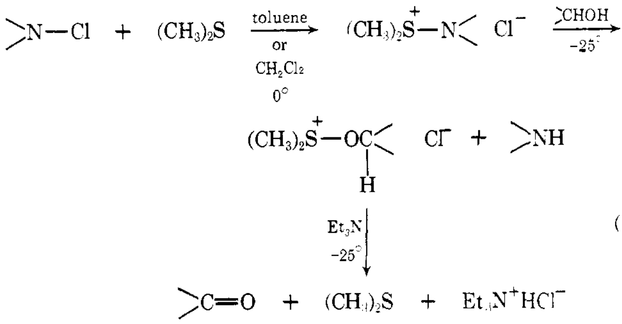
Donald G. Truhlar
Chemical Dynamics Laboratory, Department of Chemistry
University of Minnesota, Minneapolis, Minnesota 55455

Received July 21, 1972

A New and Highly Effective Method for the Oxidation of Primary and Secondary Alcohols to Carbonyl Compounds

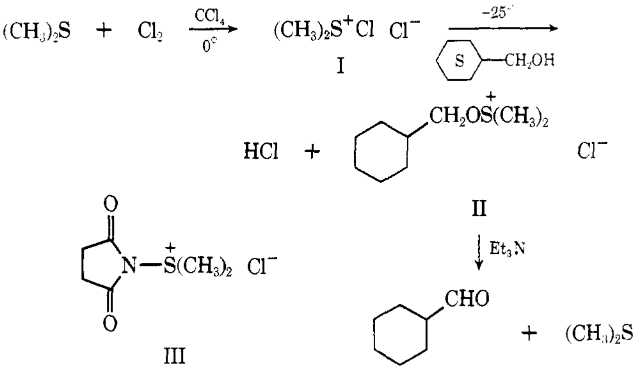
Sir:

We report here a new process for the oxidation of alcohols to ketones or aldehydes which is operationally simple, highly selective, and efficient. It is expected that the method will find widespread use and that in many instances it will be found superior to currently important procedures such as those using the reagents CrO_3–pyridine complex,[1] CrO_3–acetone,[2] and dimethyl sulfoxide with various coreactants.[3–5] An overall representation of the new method, which is clearly related to the dimethyl sulfoxide based processes, is given in sequence 1.



(1)

The long-known complexes which result from the reaction of halogens with sulfides,[6] $R_2S^+Hal\ Hal^-$, might be expected to react with an alcohol to form a type of sulfoxonium complex, $R_2S^+OCH< Hal^-$,[6b] which judging from previous work[3–5] should under suitable conditions undergo elimination to form a carbonyl compound. This process would effectively allow an overall transformation such as: $RR'CHOH + Cl_2 \rightarrow RR'CO + 2HCl$, which is mediated by a sulfide. The operability of this scheme has now been demonstrated. For example, treatment of dimethyl sulfide in carbon tetrachloride at 0° with 1 equiv of chlorine in carbon tetrachloride at 0° results in rapid formation of the partially insoluble complex I, which when cooled to −25° (Dry Ice–carbon tetrachloride bath) and treated with cyclohexylcarbinol for 2 hr at −25° with stirring is converted to the sulfoxonium complex II. Addition of 2 equiv of triethylamine, removal of the cooling bath, and isolation after 5 min affords pure cyclohexylcarboxaldehyde in *ca.* 80% yield after distillation.



The oxidation of cyclohexylcarbinol can be effected even more cleanly and efficiently (93% yield) using the recently reported complex III from dimethyl sulfide and *N*-chlorosuccinimide[7,8] under carefully controlled conditions. Most of this work has been performed using the complex III, since the use of *N*-chlorosuccinimide for small-scale laboratory work is convenient, since the formation of hydrogen chloride is avoided (in contrast to the use of I), giving a milder and probably more generally useful method, and, finally, since the reaction products are somewhat cleaner.

The simplicity and the key details of the new oxidation process are illustrated by the following procedures for the preparation of a ketone and an aldehyde.

A. 4-*tert*-Butylcyclohexanone. To a stirred solution of 400 mg (3.0 mmol) of *N*-chlorosuccinimide in 10 ml of toluene (analytical grade) was added at 0° 0.3 ml (4.1 mmol) of methyl sulfide under argon. A white precipitate appeared immediately after addition of the sulfide. The mixture was cooled to −25° (carbon tetrachloride–Dry Ice), and a solution of 312 mg (2.00 mmol) of 4-*tert*-butylcyclohexanol (mixture of cis and trans) in 2 ml of toluene was added dropwise. The stirring was continued for 2 hr at −25°, and then a solution of 303 mg (3.0 mmol) of triethylamine in 0.5 ml of toluene was added dropwise. The cooling bath was removed and after 5 min, 20 ml of ether was added. The organic layer was washed with 5 ml of 1% aqueous hydrochloric acid and twice with 15 ml of water. Removal of dried (magnesium sulfate) solvents produced 310 mg (∼100%) of 4-*tert*-butylcyclohexanone as white

---

[1] J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

[2] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946); A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *ibid.*, 2555 (1953).

[3] K. E. Pfitzner and J. G. Moffatt, *J. Amer. Chem. Soc.*, **87**, 5661 (1965); **88**, 1762 (1966).

[4] J. R. Parikh and W. von E. Doering, *ibid.*, **89**, 5505 (1967).

[5] W. W. Epstein and F. W. Sweat, *Chem. Rev.*, **67**, 247 (1967).

[6] See, for example, (a) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. II, Chemical Publishing Co., New York, N. Y., p 48, and also (b) H. Meerwein, K.-F. Zenner, and R. Gipp, *Justus Liebigs Ann. Chem.*, **687**, 67 (1965). The question of tetracovalent or sulfonium sulfur in these complexes merits further study, but is not crucial to the present application.

[7] E. Vilsmaier and W. Sprügel, *Tetrahedron Lett.*, 625 (1972).

[8] Other examples of azasulfonium salts have been reported by (a) P. G. Gassman, G. Gruetzmacher, and R. H. Smith, *ibid.*, 497 (1972), and (b) C. R. Johnson, C. C. Bacon, and W. D. Kingsbury, *ibid.*, 501 (1972). The latter group has also reported the isolation of unstable sulfoxonium salts from alcohols and the complexes of sulfides with *N*-chlorobenzotriazole.