when the pairwise group interaction parameters are adjusted to allow for the considerable polarization and increased hydrogen bonding of the water molecules in the transition state. Satisfactory slopes (SL^*_{calcd})[16] are obtained by using $G_{\mathrm{CH_2}\leftrightarrow\mathrm{OH}} = +47.5$ J·kg·mol^{-2} and $G_{\mathrm{OH}\leftrightarrow\mathrm{OH}} = -81.1$ J·kg·mol^{-2} (Table II). The plots are shown in Figure 1.

As a check for the reasonableness of the present approach, rate constants for neutral hydrolysis of **1e** were determined in 1,4-dioxane (D)–water ($m_{\mathrm{D}} = 0$–1.72 mol·kg^{-1}) at 25 °C. Rate constants decrease with increasing molality of 1,4-dioxane and a straight line is obtained by plotting ln ($k_{\mathrm{obsd}}/k_{\mathrm{obsd}}^0$) vs. m_{D}. Correlation of the data in terms of eq 4 with $n = 2$ and employing the adjusted $G_{\mathrm{CH_2}\leftrightarrow\mathrm{OH}}$ leads to $G_{\mathrm{O}\leftrightarrow\mathrm{OH}} = -30.6$ J·kg·mol^{-2}. Comparison of this value with that taken from the literature ($G_{\mathrm{O}\leftrightarrow\mathrm{OH}} = -23$ J·kg·mol^{-2})[14] shows satisfactory agreement, the augmentation will again reflect the polarization of the waters in the transition state.

In summary, the treatment based on practical pairwise group interaction parameters accounts for the general pattern of rate constants as a function of the nature and molality of the cosolvent. Further applications to other aqueous binaries as well as other reactions are under active investigation and will be given in the full paper. At this stage we conclude that the present results signal a novel and important quantitative procedure for drawing together kinetic and thermodynamic data for organic reactions in highly aqueous reaction media.

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Supplementary Material Available: Table III showing pseudo-first-order rate constants for the neutral hydrolysis of **1e** as a function of the molality of cosolvent in the ROH–H_2O and 1,4-dioxane–H_2O mixtures (2 pages). Ordering information is given on any current masthead page.

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[16] The increments in the experimental slopes (SL_{exp}) going from the C-1 alcohol to the C-4 alcohol are of the same magnitude. This is consistent with the stepwise addition of one $G_{\mathrm{CH_2}\leftrightarrow\mathrm{OH}}$ parameter in eq 4 and allows the calculation of the adjusted value of this parameter.

Reactions of H Atoms Produced by Microwave Discharge with Olefins in Acetone and Toluene

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Previous results from this laboratory have shown that microwave discharge is a convenient and effective source of oxygen atoms for organic synthesis, in condensed phases.[1] Now we report that this source also provides an excellent means of generating hydrogen atoms for the same purpose.

The reaction of H atoms with organic substrates in both liquid[2] and gas phase,[3] have been extensively studied. H atoms were generated for this purpose mainly by electric discharge of H_2, radiolysis of water and organic liquids,[2d,3] and photolysis of thiols[2b,3] and *tert*-butyl peroxyformate.[2c] In the gas phase, reactions of H atoms generally result in the vibrationally excited radicals which lead to extensive fragmentations.[3] However, in the liquid phase, the atoms were found to be less reactive.[2]

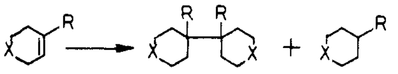
The reactions of H atoms with olefins were performed in a flow system at 2 torr, the H atoms being generated by microwave discharge (2540-MHz, 60-W output) of a mixture of H_2 and He (1:50). The discharged gases were passed over a neat liquid or a solution of the substrate.[4] Since acetone was found to be inert toward H atoms, we have used it as a solvent in these reactions.[5]

Phenyl and alkylethylenes **2** and **7** were converted almost quantitatively into the respective dimers **3**, **5**, and **8**[6,7] and hydrogenated products **4**, **6**, and **9**. No products of radical inter-

$$\underset{1}{\phi\mathrm{CR{=}CH_2}} \longrightarrow \underset{3}{\phi\mathrm{C(R)(CH_3)\,C(R)(CH_3)}\phi} + \underset{4}{\phi\mathrm{CHRCH_3}}$$

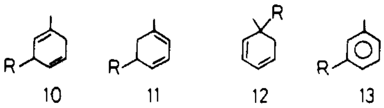
a R = H
b R = CH_3
c R = ϕ

$$\underset{2}{\phi\mathrm{CH{=}CHCH_3}} \longrightarrow \underset{5}{\phi\mathrm{CH(C_2H_5)CH(C_2H_5)}\phi} + \underset{6}{\phi\mathrm{(CH_2)_2CH_3}}$$



7 8 9

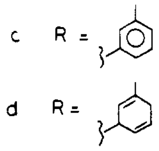
	R	X
a	ϕ	CH_2
b	H	CH_2
c	H	$(CH_2)_3$
d	H	$CH_2CH{=}CH$
e	Me	CH_2



10 11 12 13

a R = $C(CH_3)_2$ ϕ

b R = C_6H_{11}



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[4] The experimental techniques were similar to those used previously in the reactions with O(^{3}P), ref 1.

[5] The relative inertness of H atoms toward acetone is in accord with the rate constants found previously for the reactions of H atoms generated by radiolysis of water with organic substrates, cf. ref 2d.

[6] The reaction products were analyzed by GC–MS and separated by column chromatography on silica gel. The known compounds were identified by comparison with authentic samples, while the structures of the new compounds were established by MS and NMR.

[7] **3a**, found, meso/*dl* = 1.16. **5**, found, meso/*dl* = 1.20; lit.: Gibian, M. J.; Covely, R. C. *J. Am. Chem. Soc.* **1972**, *94*, 4178. Gouverneur, P. J. L.; Mukinayi Mulangala, J. *Bull. Soc. Chim. Belg.* **1977**, *86*, 699. Green, F. D.; Berwick, M. A.; Stowell, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 867. **8a**, lit.: Beckmans, H. D.; Schloch, J.; Rückhardt, C. *Chem. Ber.* **1967**, *109*, 1369. **8d**, found, meso/*dl* = 1.0; MS, *m/e* (relative intensity) 67 (100%), 55 (46), 79 (46), 94 (25), 135 (16), 162 (12), 190 (8), 218 ($M^{\cdot+}$ 1); ^{1}H NMR (90 MHz, $CDCl_3$, 7.24 ppm), δ 5.61 (m, 4 H), 2.11 (m, 4 H), 1.32 (m, 8 H); ^{13}C NMR (67.9 MHz, $CDCl_3$, 77 ppm) δ 130.5, 130.44, 44.76, 44.74, 32.87, 31.64, 30.70, 29.93, 28.74, 25.91, 25.75, 25.33, 25.22. **8e**, lit.: Liebman, S. A.; Donovan, P. F.; Koch, S. D. *J. Org. Chem.* **1962**, *27*, 4636.

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or intramolecular addition[8] to double bonds could be detected. The ratios of the dimers to the hydrogenerated products formed in the reaction of phenylethylenes **1a–c**, **2**, and **7a** were 10, 4, and 3, respectively. In the reaction of alkylethylenes, the corresponding ratios were lower: between 1.4 and 0.8 for **7b–d** and 0.3 for **7e**. Methylene derivatives **1a–c** reacted faster than all other olefins: after 30 min reaction at −78 °C, the former were converted almost completely to products, while the latter only in 40–50%.

The pattern of these reactions and the ratios of the products are consistent with the formation of radicals which undergo dimerization and disproportionation, as well as addition of H atoms.[9] We have shown that the latter two processes take place by reacting cyclohexene with D atoms and isolating cyclohexane-d_2 (40%) and -d_1 (60%), the former being mainly the product of D-addition to the cyclohexyl radical and the latter of its disproportionation.

When the reactions of H with olefins were performed in toluene, combination products of olefins and toluene were also formed. Thus, **1b** in toluene (5%) gave, after 1 h at −78 °C, 20% yield of three compounds **10a**, **11a**, and **12a**[10] in 2:1:1 ratio. They were separated after treatment with 2-phenyltriazoline-1,3-dione, resulting in adducts from which **11a** and **12a** were regenerated with KOH. Dehydrogenation of **11a** with dichlorodicyanobenzoquinone (DDQ) led to the metasubstituted toluene **13a**.[11]

Analogous three methylcyclohexadiene derivatives **10b**, **11b**, and **12b**[12] were formed (in 8:1:1 ratio) in the reaction of **7b** in toluene with H atoms. The major product **10b** was dehydrogenated with DDQ to the meta-substituted toluene derivative **13b**.[13] The formation of small amounts of dimers derived from self-condensation of hydrogenated toluene was indicated by the isolation of biphenyl derivative **13c** after dehydrogenation of the total reaction mixture.

Neat toluene also reacted with H atoms, resulting, after 30 min of reaction (ca. 1% conversion), in a mixture of dimeric products whose main constituent was a bicyclohexyl derivative **10d**.[14] It is apparent that **10–12** are thus all derived from methylcyclohexadienyl radical formed by the addition of H atom to the ortho position of toluene.

Theoretical calculation by Radom et al.[15] has shown that the latter radical is the thermodynamically most stable of the four isomeric methylcyclohexadienyl radicals. Since it was previously established that H atoms add to ortho, meta, and para positions of toluene,[16] the exclusive addition to the ortho position observed by us implies equilibration between the isomeric radicals, which occurs by elimination of H atoms, followed by their addition. Such equilibria seem reasonable in view of the reported data on the reactions of toluene and substituted toluenes with D atoms in solution[2] and on the thermal dissociation of cyclohexadienyl radical to benzene and H atoms in the gas phase.[17]

Evidence for equilibration of methylcyclohexadienyl radicals was obtained from the reaction of toluene with deuterium atoms, which results in ca. 10% of toluene-d_1 and ca. 1% of the mixture of dimeric products. We are presently investigating the scope and the synthetic application of these meta substitutions in benzene derivatives.

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(8) In the reaction of **7d**, neither bicyclo[3.3.0]octane nor the respective octene derivative were found.

(9) The ratios of the dimers to the hydrogenated products correspond to the disproportionation combination ratios of the respective radicals: Gibian, M. J.; Corley, R. C. *Chem. Rev.* **1973**, *73*, 441 and references cited therein.

(10) **10a**: MS, *m/e* (relative intensity) 91 (100%), 51 (21), 77 (78), 93 (88), 105 (82), 119 (50), 120 (62); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.1–7.3 (m), 5.75 (d, J = 10.7 Hz, 1 H), 5.45 (m, 1 H), 5.22 (m, 1 H), 3.02 (br, 1 H), 2.47 (br s, 2 H), 1.65 (s, 3 H), 1.25 (d, J = 4 Hz, 6 H). **11a**: MS, *m/e* (relative intensity) 93 (100%), 51 (18), 77 (60), 91 (99), 105 (83), 119 (58), 120 (68); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.02–7.35 (m, 5 H), 5.83 (ddd, J = 9.8, 5.2, 2.6 Hz, 1 H), 5.42 (dd, J = 13, 3.3 Hz, 1 H), 5.55 (br, 1 H), 2.7 (br, 1 H), 1.91 (m, 2 H), 1.69 (s, 3 H), 1.27 (d, J = 5 Hz, 6 H). **12a**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.1–7.4 (m), 5.55–5.82 (m, 4 H), 2.55 (dt, J = 17.5, 5 Hz, 1 H), 1.73 (dd, J = 5.2, 5 Hz, 1 H), 0.92 (s, 3 H), 1.36 (d, 6 H).

(11) **13a**: MS, *m/e* (relative intensity) 195 (100%), 77 (39), 89 (40), 91 (42), 103 (51), 165 (18), 210 ($M^{\bullet+}$, 27); ^{1}H NMR (90 MHz, CD_2Cl_2, 5.31 ppm) δ 7.22 (m, 3 H), 7.02 (m, 2 H), 2.3 (s, 3 H), 1.67 (s, 6 H).

(12) **10b**: product of reaction with deuterium atoms; ^{1}H NMR (270 MHz, $CDCl_3$) 5.75 (d, J = 10.7 Hz, 1 H), 5.62 (d, J = 10.7 Hz, 1 H), 5.33 (d, 1 H), 2.62 (br, 1 H), 2.50 (br, 2 H), 1.68 (s, 3 H), 1.14 (br, 10 H); MS, *m/e* 54 (100), 56 (11), 78 (17), 92 (49), 93 (42), 178 ($M^{\bullet+}$ 7). **11b** and **12b** identified as a mixture of endo and exo adducts with 2-phenyltriazoline-1,3-dione. **11b**: adduct a; ^{1}H NMR (270 MHz, $CDCl_3$), 7.45 (m, 5 H), 6.49 (m, 1 H), 6.28 (br s, 1H), 4.98 (br s, 1H) 1.92 (s, 3H), 0.85–2 (m, 5 H); adduct b; H NMR (270 MHz, $CDCl_3$) δ 7.5 (m, 5 H), 6.34 (m, 2 H), 5.02 (br s, 1 H), 1.92 (s, 3 H), 0.9–2.25 (m, 14 H).

(13) **13b**: ^{1}H NMR (80 MHz, $CDCl_3$) 7.53–7.02 (m, 4 H), 2.3 (s, 3 H), 1.81–0.88 (m, 11 H).

(14) **10d**: meso and *dl*; MS, *m/e* (relative intensity) 93 (100%), 91 (60), 79 (47), 77 (63), 65 (20); MS-CI (relative intensity) 187 ($MH^{\bullet+}$ 100%), 151 (25), 137 (27), 119 (10), 115 (31); ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.76 (br, 1 H), 5.31 (br, 1 H), 2.85 (br, 1 H), 2.55 (br s, 2 H), 1.69 (s, 6 H).

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Control of Stereochemistry in Five-Coordinate d^6 Complexes by Ligand Substitution

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There is overwhelming evidence from both theoretical studies[2] and solid-state structural analyses[3] that five-coordinate d^6 complexes prefer the square-pyramidal geometry over the isomeric trigonal-bipyramidal form. Thus complexes of Ru(II),[4] Os(II),[4] Rh(III),[5] and Ir(III),[6] when five-coordinate, are generally assumed to be square pyramidal in spite of the fact that solution studies rarely[7,8] provide unequivocal support for this assumption. In this paper, we detail a five-coordinate d^6 system for which both isomeric forms are observed as a function of the ligand substitution; moreover, we present a compelling diagnostic method that distinguishes between the two possible isomeric forms *in solution*.

A previous report from our laboratory outlined the preparation of the dark-green methyl halide complexes $Ir(CH_3)X[N(SiMe_2CH_2PPh_2)_2]$ (X = I, **1a**; X = Br, **1b**). These five-coordinate complexes are square pyramidal[10] both in the solid state, based on the X-ray structure of an analogue (i.e., $Ir(CH_3)I[N(SiMe_2CH_2P(i\text{-}Pr)_2)_2]$), and in solution, based on variable-temperature ^{1}H NMR studies, ligand addition reactions, and NOEDIFF[11] experiments. In particular, the observation of a positive

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