On the Mode of Reaction of Hydrogen Atoms with Organic Compounds in Aqueous Solutions[1]

ROBERT A. WITTER AND P. NETA*

Radiation Research Laboratories, Center for Special Studies and Department of Chemistry, Mellon Institute of Science, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

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Yields of hydrogen from γ-irradiated aqueous solutions of organic compounds have been determined. From these yields the portion of H atoms reacting by H abstraction has been calculated. Using previous rate data the partial rate constants for the abstraction and for the other reactions which do not yield hydrogen have been derived. Correlation of structure and partial reactivities has led to some generalized patterns of reaction. Benzylic and allylic hydrogens were found to be respectively ~3 and ~5 times more reactive in abstraction reaction than those adjacent to methyl groups. An enol site adds hydrogen atoms with a partial rate constant of $1 \times 10^8\ M^{-1}$ sec^{-1} and a carbonyl group only $\sim 10^6\ M^{-1}$ sec^{-1} so that the reactivity of carbonyl compounds is largely dependent on their enol content. Partial rate constants have also been assigned to several other functional groups.

The hydrogen atom is one of the primary products of water radiolysis and is produced with a yield of G_H = 0.6 atoms/100 eV, along with the hydrated electron ($G_{e^-_{aq}}$ = 2.8) and the hydroxyl radical (G_{OH} = 2.8).[2] Molecular hydrogen and hydrogen peroxide are also formed. Since e^-_{aq} can be efficiently converted into H

$$e^-_{aq} + H_3O^+ \longrightarrow H + H_2O \quad (1)$$

by reaction with acid, many studies on the hydrogen atom have been carried out in acid solutions, both for the sake of increasing the yield of H and for eliminating reactions of e^-_{aq} which might affect the product analyzed. A large number of papers have dealt with the reactivity of the H atom toward organic solutes and its mechanistic implications.[3] Many absolute rate constants have been determined by the *in situ* radiolysis steady-state esr method recently developed.[4] This method allows the determination of rate constants for the disappearance of H atoms upon reaction with solutes so that only the overall rates are measured with no indication of the mode of reaction. As a supplement to the previous determinations (summarized in ref 3) a set of experiments are presented here, which are devised to distinguish between the main different modes of H-atom reactions.

In these experiments the ratio between the partial rate of hydrogen abstraction and that of other reactions which do not yield H_2 is determined by measuring the yield of H_2 from irradiated solutions of various organic compounds. This yield, when corrected for the "molecular yield" of hydrogen G_{H_2} = 0.41 and compared with the total yield of H atoms $G(H) = G_H + G_{e^-_{aq}}$ under similar conditions, gives the portion of H which react by abstraction. The value of G(H) is determined by the use of compounds known to react by hydrogen abstraction only, such as isopropyl alcohol or formic acid. The overall yield of hydrogen from acid solutions of these compounds at 10^{-2} M was found to be G = 3.96 and represents the sum of G_{H_2} = 0.41 and G(H) = 3.55.[2]

Several series of compounds have been studied and the correlation between structure and mode of reaction is apparent in most cases.

Experimental Section

The organic compounds were of the purest grade commercially available (mostly from Baker, Aldrich, or Eastman) and were used without any further purification. Solutions containing 10^{-3}–10^{-2} M of the organic compound and usually 10^{-1} M $HClO_4$ were degassed on a vacuum line by six freeze–pump–thaw cycles, irradiated in a gammacell 220, and analyzed for total gas formation by a McLeod gauge and for hydrogen content by mass spectrometry. All the details of the experiments are similar to those previously reported.[5] Yield *vs.* dose plots were examined for several cases and showed linearity up to doses three times higher than usually applied.

Results and Discussion

The hydrogen yields from irradiated acid solutions of the various organic compounds studied are given in Table I. The percentage of H atoms reacting by abstraction is given by $100 \times [G(H_2) - 0.41]/3.55$. From the overall rate constant for the reaction of H determined by the esr method, the specific rate constant for the abstraction reaction is derived (last column of Table I). The difference between the rate of abstraction and the overall rate is, of course, attributed to reactions which do not yield H_2, *i.e.*, addition to a double bond, aromatic ring, or other functional group or abstraction of a halogen atom.

It can be seen from Table I that isopropyl alcohol, formic, succinic, propionic, glycolic, and glyoxylic acids all react with H atoms practically *via* abstraction only. Most of the aromatic, olefinic, cyano, and bromo compounds undergo very little abstraction. Carbonyl and chloro compounds show various intermediate values depending on their structure.

Among the aromatic compounds examined benzoic acid, nitrobenzene, and acetophenone undergo little or no abstraction at all. The 3–4% abstraction calculated for phenol, phenylacetic acid, and benzaldehyde are not highly accurate, but suggest that abstraction from these compounds can take place with a rate constant of $\sim 5 \times 10^7\ M^{-1}$ sec^{-1}. The 7% calculated for benzyl alcohol is more accurate and gives a value of 8×10^7 for the abstraction as compared to $1.1 \times 10^9\ M^{-1}$ sec^{-1} for the overall rate. Comparing the results for benzyl alcohol and benzaldehyde with the rate constants for hydrogen abstraction from ethanol ($2.6 \times 10^7\ M^{-1}$ sec^{-1}) and acetaldehyde ($2.9 \times 10^7\ M^{-1}$ sec^{-1}) one concludes that the aromatic ring

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[2] See, *e.g.*, review by M. Anbar in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience, New York, N. Y., 1968, p. 651.

[3] See review by P. Neta, *Chem. Rev.*, **72**, 533 (1972).

[4] P. Neta, R. W. Fessenden, and R. H. Schuler, *J. Phys. Chem.*, **75**, 1654 (1971).

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TABLE I

HYDROGEN YIELDS FROM γ-IRRADIATED AQUEOUS SOLUTIONS OF ORGANIC COMPOUNDS AND PARTIAL REACTIVITIES WITH HYDROGEN ATOMS

Compd[a]	$G(H_2)$[b]	Percentage of H abstraction[c]	k_H (overall),[d] M^{-1} sec^{-1}	k_H (H abstraction), M^{-1} sec^{-1}
Isopropyl alcohol	3.96	(100)	6.5×10^{7}	6.5×10^{7}
Benzoic acid	0.44	<1	1.0×10^{9}[e]	$<10^{7}$
Nitrobenzene	0.41	~0	1.0×10^{9}[e]	$<10^{7}$
Acetophenone	0.45	~1	1.2×10^{9}	$\sim 1 \times 10^{7}$
Phenol	0.51	~3	1.4×10^{9}	$\sim 4 \times 10^{7}$
Phenylacetic acid	0.54	~4	6.0×10^{8}	$\sim 4 \times 10^{7}$
Benzaldehyde	0.54	~4	1.5×10^{9}	$\sim 6 \times 10^{7}$
Benzyl alcohol	0.66	7	1.1×10^{9}	8×10^{7}
Thiophenol	2.93	71	4.0×10^{9}	2.8×10^{9}
Allyl alcohol	0.49	~2	2.5×10^{9}[f]	$\sim 5 \times 10^{7}$
cis-4-Cyclohexene-1,2-dicarboxylic acid	0.69	8	1.0×10^{9}	8×10^{7}
1-Cyclopentenecarboxylic acid	0.74	9	1.5×10^{9}	1.4×10^{8}
Cyclopropanecarboxylic acid	0.69	8	5.3×10^{6}	4×10^{4}
Cyclobutanecarboxylic acid	2.93	71	1.3×10^{7}	9.2×10^{6}
Formic acid	3.96	(100)	4.5×10^{5}	4.5×10^{5}
Oxalic acid	0.39	0	4.1×10^{5}	$<10^{4}$
Malonic acid	3.06	75	4.2×10^{5}	3.1×10^{5}
Succinic acid	3.77	95	3.5×10^{6}	3.3×10^{6}
Propionic acid	3.81	96	6.4×10^{6}	6.1×10^{6}
Glycolic acid	3.81	96	1.8×10^{7}	1.7×10^{7}
Formaldehyde	3.36	83	5×10^{6}	4×10^{6}
Acetaldehyde	3.37	83	3.4×10^{7}	2.9×10^{7}
Glyoxal	3.25	80		
Glyoxylic acid	4.01	100	2.4×10^{7}	2.4×10^{7}
Acetone[g]	2.78	67[h]	2.8×10^{6}	1.9×10^{6}
Biacetyl	1.12	20	4.7×10^{6}	9.4×10^{5}
Acetylacetone[i]	0.51	~3	8.2×10^{7}	$\sim 2 \times 10^{6}$
2,3-Dihydroxyfumaric acid	0.97	16	9×10^{7}	1.4×10^{6}
Ascorbic acid	0.48	~2	1.1×10^{8}	$\sim 2 \times 10^{6}$
Ethyl acetoacetate[j]	1.18	22	1.3×10^{7}	2.9×10^{6}
Oxaloacetic acid	0.44	~1	2.1×10^{7}	$\sim 2 \times 10^{5}$
Barbituric acid	0.84	12	2.0×10^{7}	2.4×10^{6}
Ribose	3.34	83	5.5×10^{7}	4.6×10^{7}
Acetonitrile	0.67	7	1.5×10^{6}	1×10^{5}
Trimethylacetonitrile	0.60	5	1.5×10^{7}	7.5×10^{5}
Malononitrile	0.60	5		
Cyanoacetic acid	0.84	12	3.2×10^{6}	4×10^{5}
Aminoacetonitrile (pH 1)	0.45	~1	6.6×10^{6}	$\sim 6 \times 10^{4}$
Aminoacetonitrile (pH 7)	0.76	58[k]	5.6×10^{7}	3.2×10^{7}
Methyl chloride	1.71	37	7×10^{4}	3×10^{4}[l]
Methylene chloride	1.37	27	4×10^{6}	1.1×10^{6}
Chloroform	1.13	20	1.2×10^{7}	2.4×10^{6}
Carbon tetrachloride	0.40	~0	4.8×10^{7}	
Ethyl bromide	0.51	~3	1.7×10^{8}	$\sim 5 \times 10^{6}$
Cysteine	2.84	68	4×10^{9}	2.7×10^{9}
Thiodiglycolic acid	0.41	~0	2×10^{9}	$<10^{7}$
Dithiodiglycolic acid	0.40	~0	1×10^{10}	$<10^{8}$
Nitromethane	0.41[m]	~0	4.4×10^{7}	$<4 \times 10^{5}$
Histidine	0.51	~3	4.8×10^{7}	$\sim 1.5 \times 10^{6}$

[a] All compounds have been irradiated in aqueous solutions at 10^{-3}–10^{-2} M concentration and at pH 1 adjusted with perchloric acid. [b] Given in molecules/100 eV absorbed energy. Determined from total gas formation and mass-spectrometric analysis. The accuracy of $G(H_2)$ is $\sim\pm 0.03$. [c] Calculated by $[G(H_2) - G_{H_2}]/G(H)$ taking $G_{H_2} = 0.41$ and $G(H) = 3.55$ at pH 1. The sum of these two values, 3.96, is observed for isopropyl alcohol and formic acid, which are used as references. [d] Measured by the esr method except where noted. The esr measurements reported in ref 4, 6, and 7, and by P. Neta and R. H. Schuler, unpublished data. [e] Absolute rate determined by pulse radiolysis: P. Neta and L. M. Dorfman, *J. Phys. Chem.*, **73,** 413 (1969). [f] An average value between that reported by G. Scholes and M. Simic, *ibid.*, **68,** 1738 (1964), and that reported by W. A. Volkert and R. R. Kuntz, *ibid.*, **72,** 3394 (1968). [g] 2.5×10^{-4}% enol form. [h] 65% observed in ref 5. [i] 80% enol form. [j] 8% enol form. [k] Determined by reference to isopropyl alcohol solution at pH 7 from $[G(H_2) - 0.4]/0.60$. [l] An upper limit for the rate constant of methane has been determined as $<10^{5}$ M^{-1} sec^{-1}.[4] This result and the trend that follows suggest that the upper limit for methane is probably an order of magnitude lower. [m] A yield of nitrogen of $G(N_2) \sim 0.5$ has also been observed and no mechanism for its formation is apparent.

enhances hydrogen abstraction from position α by a factor of 2–3 more than a methyl group.

In a recent correlation of the rate constants for reaction of H with aromatic compounds[6] with the substituent σ values it has been suggested that a considerable portion of H attacks the side chains of benzaldehyde and acetophenone. The present results rule out abstraction as a major contribution and assign this attack to addition to the carbonyl groups which must be activated by the ring.

The high percentage of H abstraction from thio-

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(6) P. Neta and R. H. Schuler, *J. Amer. Chem. Soc.*, **94,** 1056 (1972).

phenol and its high overall rate constant are attributed to the SH group, which is known in aliphatic compounds to undergo H abstraction with a rate constant of $\sim 3 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$.[7] The rate of abstraction from thiophenol, $2.8 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$, is in line with those values (see also result for cysteine in Table I) and the remaining rate constant of $1.2 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$, attributed to addition to the aromatic ring, is also as expected by comparison to the other aromatic compounds.

Following the above finding that abstraction from a benzylic position is enhanced only by a factor of 2–3, it is interesting to examine the effect on abstraction from allylic positions. The result for allyl alcohol does not permit an accurate comparison, but those for 4-cyclohexene-1,2-dicarboxylic acid and 1-cyclopentenecarboxylic acid can be used to estimate the reactivity of the allylic positions. Comparing the rates of abstraction from these compounds with those from cyclohexane and cyclopentane[4] and taking into account the number of abstractable hydrogens in each case, it appears that the allylic position is activated by a factor of 3 in the case of the cyclohexenedicarboxylic acid and by a factor of 10 in the cyclopentenecarboxylic acid. Obviously these are rough estimates and they suggest that enhancement of abstraction from allylic position by a factor of ~ 5 can be reasonably expected in other compounds. It should be pointed out that a similar allylic enhancement by a factor of 5 has been recently estimated for the reaction of OH with cycloolefinic compounds.[8]

Cyclopropanecarboxylic acid undergoes ring opening upon addition of H and only 8% of abstraction has been observed. With cyclobutanecarboxylic acid abstraction accounts for 70% of the reaction. The overall rate constant for the latter compound is larger than that for the first by a factor of 2.5 but the partial rate constant for abstraction is larger by over two orders of magnitude.

Oxalic acid reacts with hydrogen atoms by addition to the carboxyl groups only and no abstraction is detected. The rate constant for this addition is only $4 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$. Oxalate ions have been found to react at least an order of magnitude more slowly,[9] apparently because COO$^-$ groups have less of a double-bond character than COOH. Malonic acid also undergoes H addition to the COOH to some extent ($k \cong 1 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$) but the major reaction is abstraction from the CH_2. In succinic acid abstraction takes over completely, although an addition rate similar to that for malonic acid cannot be excluded because it would account for only 3% of the total rate.

Formaldehyde, acetaldehyde, glyoxal, and glyoxylic acid react with H atoms over 80% by abstraction. The rate constant for acetaldehyde, when compared to that for acetic acid, suggests that abstraction from the methyl group accounts for <10% of the total abstraction rate. The main reaction path in acetaldehyde, and in the other three compounds as well, is abstraction from the aldehyde group, either CHO or its hydrated form $CH(OH)_2$.

The mode of reaction with the remaining carbonyl compounds in Table I is affected by keto–enol tautomerization. Acetone undergoes H abstraction from CH_3 and H addition to CO with comparable rate constants as was previously observed.[5] The contribution of the enol form (2.5×10^{-4}%) is negligible. Biacetyl shows a slightly higher addition rate. However, acetylacetone, which is present in water 80% in the enol form, undergoes a negligible amount of abstraction and its rate constant for H addition is higher than that for biacetyl by a factor of 20. As compared with this high rate constant of $8.2 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$ the rate for abstraction from acetylacetone, although ~ 3% only, is of the same order of magnitude as abstraction from acetone and biacetyl. Similar partial rates are also observed for addition of H to dihydroxyfumaric and ascorbic acids. The results indicate that a C=C double bond bearing OH on the carbon reacts with a rate constant of $\sim 1 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$, considerably less than the rates for ethylene[4] or fumaric acid[7] ($\sim 10^9\ M^{-1}\ \mathrm{sec}^{-1}$). In agreement with this generalization, ethyl acetoacetate with 8% enol in aqueous solution exhibits a rate constant for addition of $1 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$. The rate for addition to oxaloacetic acid is $2 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$, which suggests that this compound is present ~ 20% in the enol form. The result for barbituric acid can be explained similarly.

Cyano groups add H atoms with rate constants of 10^6–$10^7\ M^{-1}\ \mathrm{sec}^{-1}$, as is seen in Table I for the nitriles examined. Aminoacetonitrile is a special case which has been examined both at pH 1 and pH 7 because the amino group in this compound has $pK_a = 5.3$. Protonation is expected to exert a large negative effect on the rate of H abstraction from the CH_2. In the acid form NH_3^+ strongly decreases the rate of abstraction to $<10^5\ M^{-1}\ \mathrm{sec}^{-1}$ and practically all H atoms add to the cyano group. In neutral solution, however, a considerable amount of abstraction is observed and the partial rate for abstraction is almost three orders of magnitude higher than that for the acid form. From the overall rate constants in acid and neutral solutions and assuming that the rate of addition remains unchanged it has been recently concluded[9] that the neutral form of aminoacetonitrile would undergo 90% abstraction. The present results show, however, that abstraction accounts for 58% only and that the rate of H addition to the cyano group increases from 6.6×10^6 to $2.4 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$ in going from the NH_3^+ to NH_2. The result for trimethylacetonitrile shows that three methyl groups also cause a similar enhancement of addition.

Halogen compounds have been studied previously[10] and found to undergo H and Cl abstraction at comparable rates but Br abstraction at much higher rates. As a result practically no H abstraction is observed with bromo compounds, as in the case of ethyl bromide in Table I. Varying percentages of H abstraction have been observed[10] with the chloro compounds depending on the partial reactivities. The results in Table I show that increased chlorination of methane causes both H abstraction and Cl abstraction to have higher rate constants.

The yield of hydrogen from cysteine solutions (Table I) is slightly lower than previously reported.[11,12] All

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(12) A. Al-Thannon, R. M. Peterson, and C. N. Trumbore, *J. Phys. Chem.*, **72**, 2395 (1968).

results show that the main reaction is H abstraction from SH.[13] The partial rate for this abstraction is 2.7 × 10^9 M^{-1} sec^{-1}, similar to that observed for thiophenol (Table I). Some abstraction of the SH group to form H_2S also takes place.[11-13] However, H abstraction from C–H bonds is negligible in cysteine. Other sulfur compounds which do not contain an SH group also react with hydrogen atoms very rapidly but in these cases no H_2 formation beyond the molecular yield is observed and the reaction must involve addition of H on the sulfur to rupture the C–S or S–S bonds as previously suggested.[7]

With nitromethane and histidine little abstraction is detected, confirming previous suggestions[4,7] based on the measured total rate constants.

In conclusion, measurement of hydrogen yields allows us to distinguish between the various modes of reaction of hydrogen atoms with organic compounds. Supplemented by rate-constant data it gives some insight into the structure of molecules. General patterns of reactivity have been summarized[3] and the present study gives additional information, mostly on the reactivities of benzylic and allylic hydrogens and of carbonyl compounds, and assigns a partial rate constant of 1 × 10^8 M^{-1} sec^{-1} for H addition to an enol site.

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Reactions of Polyarylated Carbinols. II.[1] Kinetic Study of a Suprafacial [1,5]-Sigmatropic Rearrangement[2]

Abdullatif K. Youssef[3] and Michael A. Ogliaruso*

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

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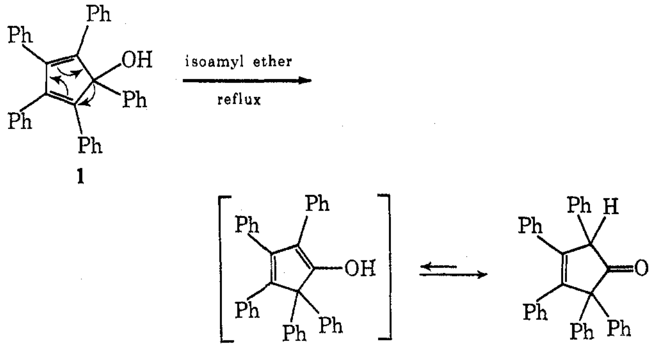
A kinetic study of the suprafacial [1,5]-sigmatropic phenyl rearrangement of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (1) to 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (2) has been performed at 173° in isoamyl ether and at 173, 180, 190, and 200° in diphenyl ether. The rearrangement is observed to be first order throughout the temperature range investigated, and the rate constants (k) at the temperatures used were found to be 0.28, 0.40, 1.09, and 2.7 × 10^{-2} hr^{-1}, respectively. Calculation of the activation energy of this phenyl [1,5]-sigmatropic shift from the Arrhenius equation gave 36.1 ± 3.6 kcal/mol, while $\Delta S^{\ddagger}$ for this phenyl migration is −7 eu. These results are used to discuss both the mechanism of this rearrangement and the transition state for rearrangement in the pentaphenylcyclopentadienol system.

Since the initial work of Mironov[4] on methyl-substituted cyclopentadienes and on 5-deuteriocyclopentadiene several thermal sigmatropic reactions of cyclopentadiene systems have recently been discovered. McLean and Haynes[5] studied the [1,5]-hydrogen rearrangement of 1-methylcyclopentadiene and 1,2-dimethylcyclopentadiene, and Roth[6] has investigated the rearrangement of isotopically labelled 5*H*-perdeuteriocyclopentadiene, while Backes[7] has reported on [1,5]-ester migrations in the cyclopentadiene system. Work on the unsubstituted indene system has been performed by Roth,[6] Alder,[8] Berson,[9] and Isaacs,[10] while Koelsch and Johnson,[11] and more recently Miller,[12] have reported studied on substituted indene systems. More recently Wawzonek[13] has reported on the thermal sigmatropic rearrangement of 3a,7a-dihydro-3,3a,5,6-tetraphenylinden-1-one. Our recent report[1] that 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (1) undergoes a thermally induced, symmetry allowed, suprafacial [1,5]-sigmatropic phenyl shift to produce 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (2) has extended these initial observations concerning sigmatropic shifts in cyclopentadiene, indene, and indenone systems to the cyclopentadienol system.

In our initial publication[1] we postulated that the conversion of 1 to 2 proceeds through the keto–enol tautomerization of the dienol intermediate 3. Since the rearrangement of 1 to 2 proceeds so cleanly and because this is the first observation of a sigmatropic phenyl shift in a cyclopentadienol system, a kinetic study of this rearrangement was undertaken to establish that this is indeed a true sigmatropic rearrangement and to obtain some information about the activation energy and the entropy of activation for this rearrangement.



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