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Some Observations on the π-Complex of Cl Atoms with Benzene

Sidney W. Benson

Contribution from the Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, California 90089-1661

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Abstract: An estimate of the entropy change in the attachment of a Cl atom to benzene together with the reported equilibrium constant led to a $\Delta H°$ for the reaction and a $\Delta_f H°$ (Ph–H:Cl) which coincides with that estimated for the chlorocyclohexadienyl radical. Kinetic considerations rule out the latter as a direct participant in chlorination. Instead its role appears to be that of a carrier for reversibly bound Cl atoms. It is in rapid cage equilibrium with the much more weakly bound π-complex which probably has never been seen spectroscopically but which still remains the most probable agent responsible for the increased selectivity of chlorination. Pyridine which has been observed[32] to be some 4-fold more selective than benzene in chlorination is shown to form a stronger complex (by 2.6 kcal/mol). However, this >N–Cl bonded complex is also not the selective chlorinating agent but rather again the more loosely bound π-complex in equilibrium with it. Effective cage concentrations of substrate RH and benzene around nascent and free Cl atoms are different as well as being different from bulk solution concentrations. An outline is given of an empirical method to estimate the thermochemistry of Cl and HCl and other gases in various solvents as a function of concentration.

Introduction

The photochlorination of alkanes (RH) by Cl_2 has long been recognized as a classic example of a two-step, radical chain reaction:

$$Cl + RH \xrightarrow{1} HCl + R^\bullet$$

$$R^\bullet + Cl_2 \xrightarrow{2} RCl + Cl$$

Both steps in the chain are extremely fast with little or no activation energy except when RH is CH_4.[1] Because of the resulting, very long chain lengths, the absolute rates tend to be very sensitive to small amounts of impurities such as O_2 and very few attempts have been made to measure them either in the gas phase or in solution. In the gas phase, measurements are further complicated by the exothermicity of the overall reaction and the accompanying heat release:

$$Cl_2 + RH \rightarrow HCl + RCl + 28\ \text{kcal}$$

The majority of the kinetic studies which have been made of the photochlorination in the liquid phase have been primarily concerned with the selectivity of the reaction toward H atoms and toward different substrates (RH). Early studies by Russell[2,3] showed a surprising effect of benzene and other aromatic solvents in increasing the selectivity of the reaction toward C–H bonds with increased substitution on C. In nearly neat benzene, compared to CCl_2H_2 as solvent, the selectivity for tertiary C–H over primary C–H was increased nearly 14-fold.

This increase in selectivity was attributed to the reversible formation of a weakly bound π-complex of the Cl atom with benzene. This weak bonding reduced the reactivity of the Cl atom and thus made it more selective. A 14-fold change in rate would correspond to a 1.6-kcal change in $\Delta\Delta G^\ddagger$ for the two reaction paths. Since these early findings much additional work has gone on with results that have both extended and complicated the initial findings. Much of this has been the subject of a recent review by Ingold et al.[4]

One of the new findings by Skell and Baxter[5] was that multiple chlorination was significant, reaching a maximum at very low substrate (RH) concentrations. This was soon confirmed[6,7] and amplified[6] together with the very reasonable suggestion that polychlorination was a consequence of the fact that step 1 in the chain following the fast step 2 was also fast enough so that there was a competition among three reaction paths for the newly liberated Cl atom, namely, diffusive separation, reaction with RH in the Cl atom solvent shell, or secondary chlorination of the product RCl which was already in the Cl atom solvent shell. This now appears to be generally accepted.[4]

A new proposal (although since disputed[4]) also by Skell et al.[8,9] was that in addition to or possibly in place of the π-complex there was also a σ-complex, the 6-chlorocyclohexadienyl radical (CCH) which was much more strongly bound and which he proposed was actually the intermediate responsible for the large enhancements in selectivity. The evidence presented was chemical in nature (from the observed formation of products with a variety of additives which suggest a CCH precursor) as well as kinetic. This followed a nanosecond photo-flash study[7] in which the authors observed a transient absorption spectrum which they assigned to the π-complex.

$$Cl + Ph\text{–}H \overset{3}{\rightleftharpoons} Ph\text{–}H{:}Cl$$

Skell et al.[9] have given arguments that the spectrum is actually that of the CCH radical. Despite subsequent rebuttals[4,10] and partial support[11] this matter is not resolved.

In their flash photolysis study, Bunce et al.[7] were able to obtain data on the rate constants k_3 and k_{-3} at room temperature. They

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(1) *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*; NASA, JPL, Pasadena, CA, 1990; No. 9. See also revised and extended version, 1992.

(2) Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 4897.

(3) Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 4997.

(4) Ingold, K. V.; Lusztyk, J.; Raner, K. D. *Acc. Chem. Res.* **1990**, *23*, 219.

(5) Skell, P. S.; Baxter, H. N., III *J. Am. Chem. Soc.* **1985**, *107*, 2823.

(6) Raner, K. D.; Lusztyk, J.; Ingold, K. V. *J. Am. Chem. Soc.* **1989**, *110*, 3519.

(7) Bunce, N. J.; Ingold, K. U.; Landers, J. P.; Lusztyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5464.

(8) Skell, P. S.; Baxter, H. N., III; Taylor, C. K. *J. Am. Chem. Soc.* **1983**, *105*, 120.

(9) Skell, P. S.; Baxter, H. N., III; Tanko, J. M.; Chebolu, V. *J. Am. Chem. Soc.* **1986**, *108*, 6300.

(10) Raner, K. D.; Luszyk, J.; Ingold, K. V. *J. Phys. Chem.* **1989**, *93*, 564.

(11) Tanko, J. M.; Anderson, F. E., III *J. Am. Chem. Soc.* **1988**, *110*, 3525.

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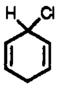
Table I. Thermochemical Data[a]

species		$\Delta_f H^\circ_{298}$ (kcal/mol)	S°_{298} (cal/(mol·K))	$C_p{}^\circ_{298}$ (cal/(mol·K))	$C_p{}^\circ_{400}$ (cal/(mol·K))	bp (K)	V_m (cm^3/mol)
Cl	(g)	28.9	39.5	5.2	5.4	120	
	(sol, 1M)	28.1	34.2*	14*	14.4		38*
C_6H_6	(g)	19.8	64.3	19.7	26.3	353	
	(sol, 1M)	12.0	47.1*	31.7*	38.3*		89
C_6H_5Cl	(g)	12.4	74.2	23.9	30.3		
	(l)	2.6	55.3	35.9*	42.3*	405	102
	(g)	26.3	69.0 ± 0.6*	22.4*	30.1*		
	(l)	18.4	46.8*	34.4*	42.1*	359	94
	(g)	16.9 ± 0.5	80.0 ± 1*	25.9*	34.8*		
	(l)	7.3	56.1*	37.9*	46.8*	411*	105*
	(g)	41.5 ± 2	80.9 ± 1.5* (84.5)	26.5*	35.4*		
	(l)	31.9 ± 2	57.0*	38.5*	47.4*	411*	108*
(CCH)	(sol, 1M)	31.9 ± 2	(61.4)	38.5*	47.4*		
HCl	(g)	–22.0	44.6	7.0	7.0	188	31
	(sol,1M)	–24.6	37.1	19.0*	19.0*		

[a] Numbers labeled with superscript asterisk are estimated, ref 12 and Appendix. Values in parentheses have had the C–Cl stretching frequency lowered by a factor of 3 from that in 3-chlorocyclohexa-1,4-diene while the two bending frequencies associated with Cl have been lowered from 400 to 220 cm^{-1}. This is probably an overestimate of the entropy by 1.5 eu.

were also able to assign rate constants to other steps in the reaction scheme including the rate constants for Cl atom atack on primary (p) and tertiary (t) H atoms as well as those for π-complex attack on p-H and t-H atoms. Of immediate interest here are their reported rate constants for k_3 and k_3 and hence for $K_3 = k_3/k_{-3}$, the equilibrium constant for formation of the optically observed complex. They reported a value at 298 K of $K_3 = 200\ M^{-1}$. From the thermodynamic relation $\Delta G = -RT \ln K$ we can then calculate that $\Delta G_3 = -3.2$ kcal at 298 K.

Some Thermochemical Observations

Bunce et al.[7] did not report K_3 at different temperatures or attempt to deduce values for ΔS_3 and ΔH_3. However, it is possible for us to estimate ΔS_3 from some simple empirical rules for the behavior of regular solutions. Let us start with gas phase species for which additivity rules allow us to estimate thermochemistry.[12] Accurate data are available for Cl in the gas phase and for benzene in both the liquid and the gas phase. These are listed in Table I. Because knowledge of the structure of the π-complex is lacking, we shall begin by taking CCH, the chlorocyclohexadienyl radical, as an approximation. Since we are primarily concerned with the entropy it will not be difficult to examine the consequences of this assumption.

With this model we deduce $\Delta S^\circ_3(300K) = -22.9$ eu for the gas phase reaction (standard states, 1 atm). To deduce ΔS°_3(sol) we need to know the entropy changes on dissolving the various species in an organic solvent consisting of benzene and CH_2Cl_2 or CCl_4. Solutions of benzene in CH_2Cl_2 and/or CCl_4 may be treated to a very good accuracy by the empirical rules which have been developed for regular solutions.[13] For such solutions, heats of mixing are of the order of 100 ± 50 cal/mol, which for our purposes are negligible. Entropies of mixing are ideal, that is, representable by eq 1:

$$\Delta S_{\text{mix}} = -R \sum_i x_i \ln x_i \qquad (1)$$

where x_i is the mole fraction of component i. For components of very different molar volumes V_i, x_i can be replaced by volume fractions, ϕ_i,[13] in eq 1.

$$\phi_i = x_i\, V_i / \sum x_i V_i \qquad (2)$$

The partial molar entropy of mixing of a solute i with solvent can then be written as:[14]

$$\Delta S_i(1M) = R \ln (1000/V_i) \qquad (3)$$

where V_i is in cubic centimeters (standard state is 1 mol/L (1 M) for the solute). To the present order of approximation it is independent of the nature of the solvent so long as the final solution is regular and the molar volumes of solutes and solvent are not too different.

The source of the data in Table I, much of which has been estimated, is discussed in the Appendix. For the moment, however, we notice that for formation of the σ-complex, in solution, $\Delta S^\circ_3 = -19.9$ eu. This is close to the gas phase value at 1 atm standard state but not as close at 1 M standard state, $\Delta S^\circ_3(1M,g) = -13.5$ eu.[12]

If we now combine our estimated value for ΔS°_3 with the observed ΔG°_3 we calculate $\Delta H^\circ_3(\text{sol},1M) = -9.2$ kcal/mol with an estimated uncertainty of ±0.6 kcal/mol.

This can be compared with the very similar value for ΔH°_3(1M,sol) estimated for the CCH radical from Table I of –8.2 ± 2 kcal/mol. Within the limits of uncertainty of the data they are the same. This would seem to imply that if there is a distinguishable π-complex then the two complexes have the same heat of formation.

Is it possible that there is a more loosely bound π-complex whose additional entropy would compensate for being more weakly bound? If we were to decrease the bonding in CCH by 1.4 kcal it would require an increase in the entropy of 4.6 eu at 300 K to compensate. However, if we decrease the already weakened force constants for Cl–C stretching and 2 ring–Cl bending modes by an additional 14% to account for this reduced binding it will only increase the entropy of the complex by about at total of 0.6 eu, not nearly enough to compensate for the reduced binding.[12]

There are data available on the binding energies of some other π-complexes with benzene, and these complexes are generally very weakly bound. One of the more studied complexes is that of molecular I_2 with Ph–H which has a binding energy of only 1.8 kcal/mol.[13] We would not expect the π-complexing of the Cl atom to be stronger.[13,16] The equilibrium constant for formation of Cl_2 π-complex with benzene has been measured as

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(12) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley: New York, 1976.

(13) Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. *Regular and Related Solutions*; Van Nostrand Reinhold: New York, 1970.

(14) Benson, S. W.; Golden, D. M. *Physical Chemistry*; Eyring, H., Ed.; Academic Press: New York, 1975; Vol. VII, Chapter 2, p 118.

(15) Reference deleted in proof.

(16) The π-bond interaction of aromatics with halogens seems to reflect weak van der Waals' forces rather than any specific chemical bonding and these will run in the sequence Cl < Br < I. See discussion in ref 13.

0.33 L/mol[17] which corresponds to $\Delta G^\circ_{298} = +0.7$ kcal/mol. If we assume that the π-complex of Cl_2 to benzene is only weakly bound by the equivalent of a slightly stronger, though localized, van der Waals' energy, then the total entropy change on forming the complex is given by the loss of translational entropy for Cl_2 (~6.4 eu) less the gain in entropy of $R \ln 4$[18] due to a decrease in symmetry of the complex from benzene and Cl_2. The net change is $\Delta S^\circ_{298} = -3.6$ eu and $T\Delta S_{298} = -1.1$ kcal/mol, leaving −0.4 kcal/mol for ΔH_{298}. This would, as expected, represent extremely weak van der Waals' binding. Increasing the entropy loss by a less plausible 5 eu to −8.6 eu would yield $\Delta H_{298} = -1.9$ kcal/mol, which would represent a probable upper limit for the π-binding. An analogous calculation for a weakly bound π-complex of Cl to benzene would yield $\Delta S^\circ_{298} = -5.0$ eu, and with the observed ΔG_{298} we find $\Delta H_{298} = -4.7$ kcal/mol, which is considerably more than a weak van der Waals' binding. The strength of π-complexes with benzene is expected to decrease in the order $I_2 > Br_2 > Cl_2$, which follows the order expected for van der Waals interactions.

Despite the argument against a π-complex bound by as much as 4.7 kcal let us consider the consequences of its existence. It would have the same free energy of binding as CCH at 298 K but differ in binding energy by 4.3 kcal. Over a temperature range of 70 °C (−14 to +57 °C) $\Delta\Delta G^\circ$ for the two complexes would change by about 1.0 kcal and their relative concentrations would change by a factor of 5. However, Bunce et al.[7] have found that the relative OD at 325 and 490 nm of the transient spectra did not change over this same temperature range. Their important conclusion was that both bands belonged to the same species.

Alternatively one could propose that the π-complex Ph–H:Cl has a binding energy of about 1.5 ± 0.5 kcal, comparable to the ΔH° value for other halogen π-complexes. Together with a ΔS° value of −5.0 eu we would obtain $\Delta G^\circ = 0 \pm 0.5$ kcal and $K_{300} = 1\ M^{-1}$. Its concentration would be about 0.5% of CCH which could account for its "invisibility" relative to CCH.[19]

The thermochemical evidence thus is unambiguously in favor of the measured equilibrium constant being that for the CCH radical and not a more weakly bound π-complex. If there is a significant concentration of π-complex in the system, the conclusion here is that its spectrum has not been measured. As we shall note later this does not rule out the existence of the π-complex. Thermochemistry leads to the conclusion that it is a metastable intermediate on the kinetic path of the free Cl atom to the much more stable but unreactive CCH radical.

The possibility that the total pool of Cl atoms is distributed among three species, CCH, π-complex, and "free" Cl, rather than two introduces new complications in the estimation of the individual rate constants in the proposed schemes. This is of particular importance for benzene concentrations in excess of 0.1 M when 95% of the Cl atom pool is present as CCH and the remaining 5% is divided between free Cl atoms and π-complex.

Reactivity of the Complex

Skell has proposed that the CCH radical is a very highly selective halogenating agent for alkanes.[5] Hence it is appropriate to consider its reactivity:

$$\dot{\mathrm{P}}\mathrm{h{-}HCl} + \mathrm{HR} \xrightarrow{5} \mathrm{Ph{-}H} + \mathrm{ClH} + \mathrm{R}^{\bullet}$$

It is first worthy of note as has already been pointed out[20] that step 5 would be unique in free radical kinetics. There is no verified example of a free radical utilizing a bound atom to perform an abstraction from a second molecule. However, if it occurs step 5 is expected to proceed via a tight transition state with an A factor of about $10^{8.5}$ L/(mol·s). If we assume that $R^\bullet$ and RH will have about the same heats of vaporization, then from the data in Table I, we can estimate that $\Delta H_{5p} = +6.4$ kcal for primary H atoms and $\Delta H_{5t} = 0$ kcal for tertiary H atoms.[21] Thus the activation energy $E_{5p} \geq 6.4$ kcal while no firm conclusions can be drawn about E_{5t} since the latter reaction is thermoneutral. We can thus estimate that $k_{5p} \leq 10^{4.2}$ L/(mol·s) at 300 K while with a lower A factor $k_{5t} \leq 10^{7.5}$ L/(mol·s). The entropy change in step 5 is so large (~22 eu) that the reverse step −5 will be negligibly slow. Both k_{5p} and k_{5t} are marginally consistent with rate constants suggested by Skell et al.[5,9] from the data of Bunce et al.[7] However the uniqueness of these reactions makes them highly unlikely.

The above estimated upper limits of k_{5p} and k_{5t} are based on the assumption of zero intrinsic activation energy. The bulk of our experience however suggests that metathesis reactions which are close to thermoneutrality are likely to have some intrinsic activation energy.[12] If this is even 1 or 2 kcal for k_{5t} and k_{5p} then both become too slow to fit the scheme proposed by Skell et al.[9] The value of k_{5p} estimated above even with no intrinsic activation energy is 100-fold slower than the value proposed by Ingold et al. (ref 4, Scheme II). The estimated value of k_{5t} marginally fits Scheme II in ref 4 but again only if it has no intrinsic activation energy.

If the CCH radical is not directly reactive on the time scale required, to what shall we attribute the reactivity and selectivity in the benzene system. The answer lies in the lability of the CCH radical. There is no barrier to the addition of the Cl atom to benzene, and since there is a longer range weak binding (1.5 ± 0.5 kcal) attributable to a van der Waals' or π-complex we can assume that the unimolecular decomposition of the CCH radical can be represented by a loose transition state with an expected A factor[12] of about $10^{14.5}$ to $10^{15.0}$ s^{-1} and an activation energy of about 7 to 9 kcal depending on the strength of the π-complex. At 300 K this would make $k_{-3} \sim 10^{7.5\pm0.5}$ s^{-1}, identical with the reported value.[7] The resulting cage complex would be expected to collapse to the more stable CCH radical with a rate constant of about 10^{10} s^{-1}. However, it could also separate with a diffusion rate constant of about the same order. But most important, if it were to find a substrate molecule in its cage wall it could find a competing path for H abstraction also with about the same order of rate constant. The residual 1–2 kcal binding to the aromatic could account for the selectivity shown. Note that the maximum selectivity enhancement found in 2,3-dimethylbutane of a factor of about 31 for C_t–H over C_p–H (k_t/k_p) corresponds to $\Delta\Delta G^\ddagger = 2.0$ kcal for the rate difference in the two paths, a relatively small value and about the range we would expect for weak π-binding.

It is important to realize that with $K_3 = 200\ M^{-1}$ the concentration of "free" Cl atoms is less than 0.5% of the pool of weakly bound Cl species when (Ph–H) = 1 M. When (Ph–H) = 10 M these free Cl atoms plus π-complex are only 0.05% of the Cl pool.[22] Nevertheless, under these conditions all reactions of Cl must be attributed to the metastable π-complex. Note that when (Ph–H) ≥ 1 M any decomposing CCH radical will form a π-complex with, on the average, one additional Ph–H molecule in its cage. We expect its lifetime toward CCH formation to be appropriately lowered. Even at 0.1 M Ph–H only 5% of the Cl

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[17] Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1951**, *73*, 462.

[18] This assumes that the Cl_2·benzene complex has an external symmetry of 6 (centrally located Cl_2 molecule perpendicular to the ring).

[19] We are assuming that both bands belong to the same species.

[20] Walling, C. *J. Org. Chem.* **1988**, *53*, 305.

(21) The values quoted for ΔH_{5p} and ΔH_{5t} ignore the solvation energy of HCl which would make each of them more exothermic by an additional 2.5 kcal/mol. This 2.5 kcal/mol arises from the more favorable solvation enthalpy of HCl in solution relative to the Cl atom. We have ignored this extra solvation enthalpy of HCl since it arises from the contribution of the dipole moment of HCl to its greater heat of vaporization vis-a-vis Cl atom. One would not expect this dipole and solvation interaction would be achieved prior to reaction or in the transition states of reactions. If it is, then the upper limits on the rate constants must be appropriately relaxed.

(22) In this range of concentration every "free" Cl atom will have between 1 and 9 benzene molecules in its solvent cage. It is hard even to visualize what is meant by "free" Cl atoms under such conditions.

species will exist as "free" Cl atoms and 95% as CCH and about 0.5% as π-complex (assuming $K(\pi) = 1\ \mathrm{M}^{-1}$).

Because of the long chains, effectively all Cl atoms are born in step 2 of the chain by the fast exothermic reaction of $R^{\bullet}$ with Cl_2. Hence as has been pointed out[7] these Cl atoms are formed in a cage along with a RCl molecule. In the absence of any other species in the cage, diffusion out of the cage can compete with further reaction with RCl. Both of these paths are comparable in rate. The picture is further complicated by the fact that the approximately 25 kcal of exothermicity of step 2 is shared between Cl and RCl[23] and dissipation of this energy if translational although fast is only about 30-fold faster than diffusion. Finally when Ph-H or RH_2 can exist in the cage as well, all paths become competitive. Such a picture has been shown to account for the chlorination behavior of 2,3-dimethylbutane[5] as well as of neopentane and cyclohexane.[9]

The particular significance of the CCH radical is that, once it is formed, its diffusion out of cages is much faster than its decomposition back to the weakly bound π-complex. Thus CCH is a good transport vehicle for the Cl atom. However, when it does eventually decompose to yield π-complex in a cage the situation becomes more complicated than has been presented by the usual cage-diffusion models. CCH is in near equilibrium with the π-complex, and this relation is only destroyed when the Cl atom and Ph–H diffuse out of their mutual cage.[24]

A consequence of the fact that benzene remains in the initial cage formed from the decomposition of the CCH radical is that the effective initial cage concentration of benzene is greater than the concentration of benzene in the bulk solution. Let us assume that $(\mathrm{Ph{-}H})_0$ is the concentration of benzene in neat (or pure) benzene and (Ph–H) is the bulk concentration when it has been diluted by other solvents and reagents. Then the cage concentration of Ph–H immediately after the decomposition of CCH is given by:

$$(\mathrm{Ph{-}H})_c = \frac{1}{Z}(\mathrm{Ph{-}H})_0 + \frac{(Z-1)}{Z}(\mathrm{Ph{-}H}) = (\mathrm{Ph{-}H}) + \frac{1}{Z}\{(\mathrm{Ph{-}H})_0 - (\mathrm{Ph{-}H})\} \qquad (4)$$

where Z is the average number of near neighbors in the solution. Since $Z \sim 10$ in van der Waals liquids and $[\mathrm{Ph{-}H}]_0 \sim 11.4$ M it can be seen that there is a considerable correction to cage concentrations when (Ph–H) concentrations fall below that of pure benzene. In the same way there is a correction to the possibility of having other solute species in the cage because of the presence of one molecule of Ph–H already in the cage. For reactive solute molecules RH, their probability of constituting one of the cage molecules when CCH decomposes is given by their effective cage concentration:

$$(\mathrm{RH})_c = \frac{(Z-1)}{(Z)}(\mathrm{RH}) \qquad (5)$$

Such considerations will modify some of the simple methods of plotting selectivity against concentrations that have been employed.[4,5,7–9,11] The picture of the reaction that emerges from this view is not very different from those outlined in the mechanisms by Skell et al.[9] and by Bunce et al.[7] The latter have shown that the results can be accounted for with only two active intermediates, which they presume to be free Cl atoms and the π-complex. The mechanism of Skell et al. differs from this only in assigning a dominant role to CCH and assuming the π-complex is only slightly more selective than free Cl atoms and has almost as fast a rate constant. He could equally well have dropped the contribution of the π-complex without altering the fit of his equation to the data.

The reaction of CCH and RH we now see can be equally well interpreted as a unimolecular decomposition of CCH in a cage possibly containing RH.[24] The newly liberated Cl is still weakly attracted by its parent benzene and thus forming the true and selective π-complex. This weakly bound Cl can now react with RH with high selectivity, return to form CCH, or escape from the cage to form free Cl. Only small changes in the originally assigned rate constants are needed to yield the same results. We shall not attempt that here.

Alternative Reactions of the CCH Radical

If the dominant radical is CCH then it is of interest to ask why it does not react rapidly with Cl_2 to form $C_6H_6Cl_6$. In fact it can react[9] but at a slower rate than the rate with which it decomposes to liberate Cl atoms. There is no great driving force for the reaction. In the gas phase the reaction:

$$\mathrm{CCH} + \mathrm{Cl_2} \xrightarrow{6} \mathrm{ClCCH} + \mathrm{Cl}$$

is estimated to be only 5 kcal/mol exothermic. In solution it is estimated to be about the same. In the gas phase the more exothermic reaction ($\Delta H = -12$ kcal) of $CCl_3 + Cl_2$ has an activation energy of 5.3 kcal,[25] making it very slow. The delocalized radical CCH probably reacts relatively slowly with Cl_2 for comparable reasons.

Bunce et al.[7] have measured an effect of increasing Cl_2 concentrations on the rate of formation of the π-complex which they attribute to the reaction:

$$\mathrm{Cl} + \mathrm{Cl_2} \xrightarrow{11} \mathrm{Cl_3}$$

where Cl_3 is chemically unreactive on the time scale of their experiments. A thermochemical analysis of this reaction would show that for this to be true $-\Delta H^{\circ}_{11} \geq 11$ kcal, a very unlikely result.[26]

However, Skell et al.[9] have shown that in competitive experiments of neopentane (0.05 M) and benzene (10 M), hexachlorocyclohexane is produced relative to neopentyl chloride at a rate that increases proportional to Cl_2 concentration. Assuming that CCH reacts with Cl_2 Skell then estimated the rate constant as 3×10^7 L/(mol·s). Since only the π-complex can react with neopentane, this estimate requires a knowledge of the amount of π-complex in the system which is not independently available. Note however that Bunce et al.[7] have estimated a rate constant of 5×10^8 L/(mol·s) for k_{11}. If however their Cl_2 effect is attributed not to reaction 11 but to reaction 6 of CCH with Cl_2 which would also appear to enhance growth rates for the production of transient with increasing Cl_2 then we would require a rate constant of about 3×10^8 L/(mol·s) for CCH + Cl_2, a value not inconsistant with Skell's estimate.[27]

It has been argued that this reaction would lead to dichlorocyclohexa-1,3-diene (DCCH) + Cl which would not deplete Cl atoms in the system.[7] However it must be recognized that DCCH and Cl would be formed in the same cage and secondary addition to form the allylic c-$C_6H_6Cl_3$ radical would be as fast as the

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[23] Reference deleted in proof.

[24] Cleavage of the C–Cl bond in the CCH radical leads to a Cl atom above its former C-atom partner in the benzene ring. The π-complex presumably has the Cl atom above the center of the benzene ring. The change from one to the other involves a diffusive displacement of about 1.4 Å.

[25] Kerr, A.; Moss, S. J. *Handbook of Bimolecular and Termolecular Gas Reactions*; CRC Press: Boca Raton, FL, 1981; Vol. I, p 272.

[26] There have been innumerable but unsuccessful efforts to observe a Cl_3 species in the gas phase and in solution. If it existed it would play an important role in the recombination of Cl atoms. Such an effect has been observed for O_2 which does form a weakly bound complex with $DH^{\circ}(\mathrm{Cl{-}O_2}) \approx 7$ kcal but not for Cl_2 [see ref 31 and discussion on p 343 in: Benson, S. W. *Foundations of Chemical Kinetics*; McGraw Hill: New York, 1960].

[27] From Skell's data I estimate that the reaction of CCH with Cl_2 is about 6.5×10^{-3}-fold slower than neopentane with Cl. If we assume that the rate of reaction of neopentane with Cl is the same as that of Cl with dimethylbutane at the primary position (both have 4 methyl groups), then I estimate using Bunce's value[7] of $2 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ a value of $1.3 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$ for CCH with Cl_2. The authors' estimate is $5 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$.

reaction of Cl with benzene. The allylic radical could react with Cl_2 to continue the chlorination, but cage reactions would be constantly competing with release of nascent Cl atoms. Note also that the reaction of the allyl radical with Cl_2 is only about 11 kcal exothermic and is expected to be slower than the rate of reaction of alkyl radicals with Cl_2.

There appears to be some dispute about the reaction of CCH with O_2. Skell et al.[9] report a reaction which produces Ph–Cl but at a relatively slow rate, 6.3-fold slower than that of the cyclohexadienyl radical plus O_2 which gives HO_2 + benzene. Using the reported value for the latter[28] would give about 2.6×10^8 L/(mol·s) for the former. This would seem to imply a deactivating effect in CCH of Cl on H when compared with the very rapid reaction of cyclohexadienyl radical with O_2. Skell et al.[9] have suggested that this is a consequence of the high spin density on Cl in contrast to the ipso H, and this is not unreasonable.[29] The gas phase reaction of O_2 with CH_3O to form $HO_2 + CH_2O$ is as exothermic as either the reaction of CCH or cyclohexadienyl radical with O_2 and yet it is very slow.[30] Further complicating such comparisons is the fact that the reaction of O_2 with CCH or cyclohexadienyl is likely to proceed via a reversible addition to the ring rather than direct metathesis. We can estimate that $\Delta H = -10.5 \pm 2.0$ kcal/mol for addition of O_2 to cyclohexadienyl radicals. This is expected to be smaller for CCH since the addition is likely to be in the ortho position where the O_2 is in the β position to the Cl atom, which is an energetically unfavorable position for two electrophilic species. If O_2 added in the para position cis to the H atom, their separation would be about 3 Å while a tight transition state would require a 1.3 Å distance. Consequently an appreciable strain could be involved. In either case the reverse dissociation is reasonably rapid with parameters not much different than those for dissociation of CCH. Still further complicating the picture is the fact that $ClOO^\bullet$ has a bond strength (BDH) of about 5 to 6 kcal in the gas phase[1,31] and an estimated value of about 10 to 11 kcal in solution. Consequently O_2 could exothermically abstract Cl from CCH!

Some Other Complexes

Breslow et al.[32] have reported that pyridine (Py) is 4-fold more selective than benzene in the reaction of 2,3-dimethylbutane with Cl ($k_t/k_p = 200$ at 4 M pyridine). Using the same experimental techniques as Bunce et al.[7] they find a transient absorption with $\lambda_{max} = 334$ nm and no visible spectrum. Its formation rate constant is 1.5×10^{10} M^{-1} s^{-1} which is about 6 times faster than that found for CCH in benzene.[7] Its dissociation rate was 2.6×10^5 M^{-1} s^{-1} giving an equilibrium constant for the reaction

$$\mathrm{Py} + \mathrm{Cl} \overset{3'}{\rightleftharpoons} \mathrm{Py{:}Cl} \quad k_3'(298\mathrm{K}) = 3.4 \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$$

$$\text{and } \Delta G^\circ{}_3',(298\mathrm{K}) = -6.2\ \mathrm{kcal/mol}$$

Using data on the heat of formation and entropy of liquid pyridine[33] and using the Breslow et al. finding that the complex with Cl is a weakly bound N–Cl radical similar in structure to chlorobenzene it is found that $\Delta S^\circ{}_3'(1\mathrm{M}) = -15.7$ eu, somewhat less negative than $\Delta S^\circ{}_3$. This then gives $DH^\circ{}_3' = -10.9$ kcal/mol, making the N–Cl bond stronger than the C–Cl bond in CCH by 1.7 kcal/mol. An *ab initio* calculation[32] yielded an N–Cl bond strength (gas phase) of 5.1 kcal/mol in the complex. This is probably within the limits of accuracy expected for such a calculation and so in reasonable agreement with the experimental value. What is of special interest is the absence of a visible spectrum for the complex of the type observed for CCH. Since K_3 and K_3' differ by a factor of 170 one might expect that in 4 M pyridine there would be a CCH type structure with a concentration smaller than that of the N–Cl structure by a factor of $K_3'/K_3 = 170$. This supports our earlier estimate that a true π-complex structure of Ph–H:Cl would have a concentration about 200 times less than the more tightly bound σ-radical and thus be "invisible".

Further support for such a conclusion comes from the observation[32] that when 2,6-di-*tert*-butylpyridine is used the complex shows two absorption maxima—one at 325 nm and the other at 420 nm in the visible. This was interpreted as due to a CCH type structure, the substitution preventing bonding of Cl atoms to the N atom in the ring. Also noted was the fact that this substituted pyridine showed less selectivity than benzene. This might be a consequence of the fact that it probably binds Cl less strongly than benzene.

The Py:Cl σ-bound radical being more strongly bound than the CCH radical is even less likely to engage in a direct bimolecular attack on hydrocarbon. The authors[32] have proposed that in 5 M Py essentially all of the reaction with 2,3-dimethylbutane (DMB) is with the Py:Cl σ-complex. For the same reasons outlined for CCH we should like to suggest that it is a spectroscopically unseen π-complex of pyridine and Cl that is responsible for the selective chlorination of DMB. And again, without additional more direct knowledge of the equilibrium constant for formation of the π-complex we cannot establish accurate constants for its rate constant. The factor of 4 greater selectivity compared to benzene would correspond to a 0.8 kcal difference in $\Delta G^\ddagger$ for the two π-complexes Ph–H:Cl and Py:Cl. Since the $\Delta S^\ddagger$ are likely to be the same for the two we would have to attribute it to the differences in $\Delta H^\ddagger$ for the formation of the two π-complexes. This is in accord with their heat of vaporation difference which at 298 K is 1.4 kcal greater for pyridine than for benzene.[33]

Spectroscopic Data

Bunce et al.[7] and later Ingold et al.[4] have put great weight on the spectrum of the Ph–H:Cl intermediate as being that of the π-complex. In support of this conclusion they compared it with the spectrum of the cyclohexadienyl radical which has an equally strong but narrow absorption peaking at 320 nm in the UV and a 30-fold weaker but broader absorption in the visible from 490 to about 565 nm. By contrast, Ph–H:Cl has a strong, broad absorption starting at 320 nm and extending to shorter wave lengths and a weaker absorption in the visible peaking at about 490 nm but extending from about 400 to 700 nm.

Skell et al.[9] have argued that a strong coupling of the weakly bound Cl in CCH to the π-system could well account for the visible features and an increase in intensity in CCH compared to the cyclohexadienyl radical. Note, however, that the C–H bond in the cyclohexadienyl radical is about 22 kcal/mol compared to only 9 kcal/mol for the Cl in CCH. An interesting comparison comes from a complex of the ethyl radical with pyridine[32] which shows three peaks in its spectrum at 304, 395, and 632 nm. It can be estimated that this complex corresponds to an ethylpyridyl radical similar to CCH with an >N–Et group in place of >C-(H)(Cl). The estimated N–Et bond strength is 10.5 kcal, only 1.3 kcal stronger than the C–Cl bond in CCH. Breslow et al.[32] consider this a "fully-developed" σ-bond.

If we consider the visible spectrum of CCH as being that arising from an "internal" charge transfer complex, the usual calculation

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(28) Maillard et al. (Maillard, B.; Ingold, K.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095) report a value of 1.6×10^9 M^{-1} s^{-1} for O_2 with the cyclohexadienyl radical in benzene solution.

(29) A referee has suggested that the hydroxycyclohexadienyl reacts with O_2 at about the same rate as does cyclohexadienyl, and since OH and Cl have about the same electronegativity, CCH and the hydroxy radical should be comparable. However, this ignores the fact that the C–OH bond is 10 kcal stronger than the C–Cl bond so that thermochemically the hydroxycyclohexadienyl radical is much closer to the binding in cyclohexadienyl itself. Note also that the electron affinity of Cl is 3.6 eV while that for OH is only 1.5 eV.

(30) Barker, J. R.; Benson, S. W.; Golden, D. M. *Int. J. Chem. Kinet.* **1977**, *9*, 31. See also ref 1.

(31) Buss, J. H.; Benson, S. W. *J. Chem. Phys.* **1958**, *28*, 301.

(32) Breslow, R.; Brandl, M.; Hunger, J.; Turro, N.; Cassidy, K.; Krogh-Jesperson, K.; Westbrook, J. D. *J. Am. Chem. Soc.* **1987**, *109*, 7204.

(33) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Thermochemistry of Organic Compounds*; Wiley & Sons: New York, 1969.

would have to be corrected for the strain introduced by the nonplanar C–H bond. A crude estimate places this at about 2 eV while an additional correction for the too close Cl^-–H distance and the loss of the initial covalent bond (8.6 kcal) would bring this very close to the observed 2.55-eV peak. The simple model of the charge transfer bond with correction for initial bonding (E_0) and strain (E_{st}) is:

$$h\nu_{CT} = I_D - E_A - W + E_0 + E_{st}$$

where I_D is the vertical ionization potential of the donor, E_A is the electron affinity of the acceptor, and $W = e^2/r_{AD}$ is the Coulombic energy of the ion pair separated by the distance r_{AD}, e being the unit electronic charge.

Bunce et al.[7] and Raner et al.[10] have had difficulty in qualitatively accounting for the visible aromatic halogen atom spectra. In a series of different aromatic donors, the Ar:Cl complex shows no correlation of $h\nu_{CT}$ with I_D over a range of 1.5 eV in I_D. This is in contrast to the spectra of Ar:I complexes for which $h\nu_{CT}$ correlates reasonably well with I_D. A further difficulty has escaped comment up to now, namely that $h\nu_{CT}$ values for Cl and I atoms are almost the same with benzene as donor whereas the electron affinity differences between Cl and I atoms (0.56 eV) and the difference in radii of Cl and I atoms (~0.4 Å) would indicate that $\Delta(h\nu_{CT})$(Cl–I) should be about –0.72 eV for all donors. Note that Br and I atoms can only form π-complexes with benzene, the σ-complexes being unstable.[34]

Conclusions

Thermochemical evidence favors very strongly the identification of the transient visible and near-UV spectrum seen in chlorination in benzene as belonging to the very labile 6-chlorocyclohexadienyl (CCH) radical. This radical appears to be in very rapid equilibrium with the much more weakly bound π-complex of Cl with benzene.

Kinetic evidence strongly favors a weakly bound π-complex as the chlorination agent responsible for the higher selectivity shown in benzene-containing solutions. It is highly unlikely that the CCH radical plays any direct role in the chlorination process. It has a half-life of about 30 ns with respect to dissociation and can form a weakly bound, labile, peroxy radical with dissolved O_2.

Almost all reactions in the systems are very rapid, close to the diffusion-controlled limit. These include secondary chlorination by the nascent Cl atom and reaction of this atom with substrate RH to form HCl + R$^\bullet$ or with benzene to form CCH. In benzene containing solutions the cage concentrations of benzene around Cl atoms will be appreciably higher than random while the cage concentrations of substrate RH will appear to be less. For nascent Cl atoms arising from reaction step 2, the cage concentrations of both RH and benzene will be smaller than that in the bulk solution. This latter consideration is further tempered by the fact that the ratio of free Cl_2 to benzene-complexed Cl_2 is less than 1 for (Ph–H) > 3 M.

The greater selectivity (4×) seen in the pyridine system compared to benzene is similarly attributed to an unseen π-complex of pyridine with Cl.

Appendix: Solubility of Gases

In order to apply the regular solution model to mixtures of gases and liquids we need to construct a thermodynamic cycle as follows.

For gas A dissolving in liquid L, we start with 1 mol of the gas at its boiling point (T_A) in equilibrium with liquid A:

We take N mol of liquid solvent L at 298 K and cool/heat it to T_A as needed. N mol is the amount of L needed to form a 1 M solution when mixed with 1 mol of A at 298 K. We assume L remains liquid, supercooled if necessary at T_A. Since we are concerned generally with gases at room temperature dissolving in liquid whose boiling points are generally above room temperature, T_A < 298 K and cooling is the usual process.

$$\begin{tikzcd}
A(g, 1\ atm, 298\ K) \arrow[r, "1", "\substack{\Delta S_1 = \overline{C_{pg}} \ln(T_A/298); \\ \Delta H_1 = \overline{C_{pg}}(T_A - 298)}"'] & A(g, 1\ atm, T_A) \arrow[d, "2"', "\substack{\Delta S_2 = -20\ eu; \\ \Delta H_2 = -\Delta H_{vap}(T_A)}"] \\
 & A(l, 1\ atm, T_A) \arrow[d, "3"', "\substack{\Delta S_3 = R \ln(1000/V_A); \\ \Delta H_2 = \Delta H_{mix} = 0 \\ (see\ text)}"] \\
A(sol\ L, 1\ M, 298\ K) & A(sol\ L, 1\ M, T_A) \arrow[l, "4"', "\substack{\Delta S_4 = \\ -\Delta S_1 - \Delta S_6 - 12 \ln T_A/298)}"] \\
N\ mol\ of\ L\ (liq), 298\ K \arrow[r, "6", "\substack{\Delta S_6 = N\overline{C_{PL}} \ln(T_A/298); \\ \Delta H_6 = N\overline{C_{PL}}(T_A - 298)}"'] & N\ mol\ of\ L\ (liq), T_A \arrow[u, "5"', "\Delta H_4 = -\Delta H_1 - \Delta H_6 - 12(T_A - 298)"]
\end{tikzcd}$$

At T_A we can take $\Delta S_A(T_A) = \Delta H_{vap}(A)/T_A$ so that if we know $\Delta H_{vap}(A)$ we can estimate ΔS_A. Since this is not possible for gases such as Cl atoms we need to estimate both ΔH_{vap} and the boiling point. If we can estimate ΔH_{vap} then it is possible to estimate T_A by using Trouton's rule that $\Delta S_A(T_A) \approx 20$ cal/(mol·K). For Cl atoms we assume only van der Waals' forces will operate in the hypothetical pure liquid Cl. We can estimate the van der Waals' energies by assuming that it is about one-half the van der Waals' energy of Cl_2. Since the heat of vaporization of Cl_2 is 4.8 kcal/mol this would give us 2.4 kcal/mol for the ΔH_{vap}(Cl) and from the Trouton relation we estimate 120 K as the boiling point of this hypothetical Cl liquid. For comparison, Ar with a higher ionization potential and therefore weaker van der Waals' forces has ΔH_{vap} = 1.8 kcal and a boiling point of 87 K compared to an estimated 90 K from Trouton's relation. Another comparison would be HCl which has a boiling point of 188 K and ΔH_{vap} = 3.8 kcal/mol. It will have about the same van der Waals' forces as Cl but in addition a significant dipole contribution to ΔH_{vap}.

The heat of mixing is always positive and usually small for liquids whose energies of vaporization per cubic centimeter are close. The Hildebrand solubility parameter $\delta_i = [\Delta E_v/V_i]^{1/2}$ is a measure of ΔH_{mix}. When δ_i is very different for solute and solvent as it will be for the hypothetical Cl atom liquid and CH_2Cl_2 or benzene then ΔH_{mix} may approach 0.5 kcal/mol.[13] We shall ignore this here. We shall assume that the energy required to heat the 1 M solution from T_A to 298 is a sum of two terms, the energy to heat the solvent L and that required to heat the solute A. The solvent term is cancelled by the energy removed in cooling the pure liquid L and the solute term is partially cancelled by the energy required to cool gas A from 298 K to T_A. Liquids have a heat capacity generally 12 cal/(mol·K) greater than their gases, and for monoatomic liquids this is apt to be closer to 9 eu since they have no torsional contributions to C_p but only librational terms and an expansion term.[14] Applying this to benzene gas we estimate by this cycle that $\Delta_f H(1,298)$ = 12.0 kcal/mol. The measured value is 11.7 ± 0.2 kcal/mol.[35]

This is the model we have used to estimate the thermochemical terms in Table I. The errors are unlikely to exceed 1 kcal in ΔG.

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[34] Using similar methods of estimation it is found that the bromocyclohexadienyl radical is about 7 kcal unstable toward dissociation while the iodocyclohexadienyl radieal is about 24 kcal unstable.

[35] Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: New York, 1986.