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Time-Resolved Studies of the Reactions of CN Radical Complexes with Alkanes, Alcohols, and Chloroalkanes†

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Ultrafast transient absorption experiments monitor the reaction of CN radicals with 16 different alkane, alcohol, and chloroalkane solutes in CH_2Cl_2 and with a smaller number of representative solutes in $CHCl_3$ and CH_3CCl_3. In these experiments, 267-nm photolysis generates CN radicals, and transient electronic absorption at 400 nm probes their time evolution. A crucial feature of the reactions of CN radicals is their rapid formation of two different types of complexes with the solvent that have different stabilities and reactivities. The signature of the formation of these complexes is the CN transient absorption disappearing more slowly than the infrared transient absorption of the HCN product appears. Studying both the growth of HCN and the decay of the CN−solvent complexes in the reaction of CN with pentane in CH_2Cl_2 and $CHCl_3$ solutions provides the information needed to build a kinetic model that accounts for the reaction of both complexes. This model permits analysis of the reaction of each of the 16 different solutes using only the decay of the CN transient absorption. The reaction of CN−solvent complexes with alkanes and chloroalkanes is slower than the corresponding reactions of Cl. However, the reactions of alcohols with both CN and Cl occur at about the same rate, likely reflecting additional complexation of the CN radical or its ICN precursor by the alcohol. The rates for the reactions of CN with the chloroalkanes decrease with increasing Cl content of the solute, in keeping with previous observations for the reactions of Cl in both gases and liquids.

I. Introduction

Ultrafast studies of the rates and dynamics of bimolecular reactions in solution and their comparison with reactions of gas-phase molecules reveal differences and similarities of reactions in the two environments. Observing the loss of reactants and the appearance of products on a time scale that is comparable to the encounter time in solution reduces ambiguities arising from secondary reactions and can, in favorable cases, reveal new details about the reacting species. For example, a recent study of the reaction of CN radicals with several chloroalkane solvents shows that two complexes with very different reactivities form rapidly and control the chemistry.[1] Here we extend that work to include reaction with a variety of added solutes to understand the reactivity of the complexes formed between CN radicals and solvent molecules.

The CN radical is an attractive species for ultrafast spectroscopic studies. It is possible to generate it in solution by 267-nm photolysis of ICN and to probe both it and the HCN reaction product using transient absorption near 400 nm and 3.07 μm, respectively. One of the first ultrafast studies of bimolecular reaction in solution probed the HCN and ClCN products of the reaction of CN with $CHCl_3$ using transient infrared absorption.[2] Two other studies followed the fate of photolytically generated CN radicals in solution by transient electronic absorption near 400 nm and observed two decay times that they assigned to recombination and reaction.[3,4] Our recent study of CN radical reactions followed both the decay of the transient absorption of the CN radical and the growth of the transient absorption of the HCN reaction product in seven different chloroalkane solvents. It showed that the HCN absorption appeared between a factor of 2.5 and 12 times more rapidly than the CN absorption disappeared, depending on the identity of the solvent.[1]

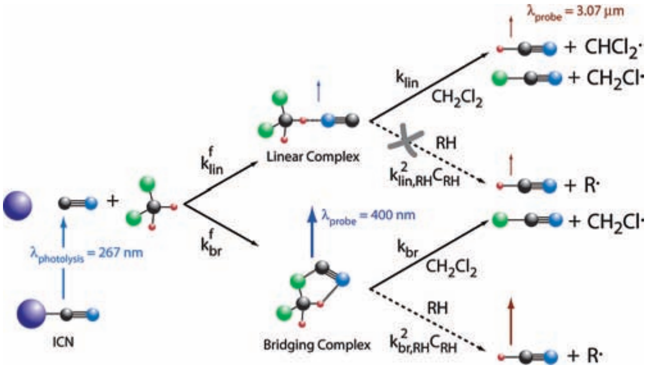

Figure 1. Kinetics scheme for reaction of CN radicals in CH_2Cl_2. After 267-nm photolysis of ICN, the CN radical rapidly forms a linear complex with a rate constant k^f_{lin} and a bridging complex with a rate constant k^f_{br}. The linear complex can abstract hydrogen or chlorine from the solvent with a first-order rate constant k_{lin}, and the bridging complex can abstract a chlorine from the solvent with a first-order rate constant k_{br}. Each of these complexes can also abstract a hydrogen, or chlorine in chloroalkane solutes (not shown in the scheme), from a solute with second-order rate constants $k^2_{lin,RH}$ and $k^2_{br,RH}$, respectively. The size of the arrows for the probe transitions reflects the transient absorption signal strength. The "x" on the pathway for abstraction of hydrogen from the solute by the linear complex indicates that it contributes only a minor part of the HCN signal.

This behavior points to a decoupling of the loss of CN and the formation of HCN that results from rapid formation of two different complexes of CN with the solvent. The kinetic scheme in Figure 1 shows those two complexes, which react at different rates and do not interconvert on the time scale of their reactions. The more weakly bound, less abundant linear complex reacts

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rapidly with the solvent to form most of the HCN, and the more strongly bound bridging complex reacts slowly to form primarily ClCN. Consequently, most of the slowly decaying transient electronic absorption comes from the dominant bridging complex, and the rapidly growing HCN absorption comes from reaction of the linear complex. Several other studies of condensed phase reactions of radicals implicate complexes as well. For example, complexes involving Br radicals are important in a variety of different systems,[5−7] and weak complexes of Cl radicals play a role in the reaction of Cl in CH_2Cl_2 and CCl_4 solutions.[8−10] One of the first illustrations of the involvement of complexes in bimolecular reactions in solution is a study showing that π-complexes between Cl and aromatic molecules influence the chlorination of 2,3-dimethylbutane.[11]

Previous ultrafast studies of the reactions of Cl atoms with alkanes, alcohols, and chloroalkanes[9,10] are a useful point of comparison for the reactions of CN that we describe here. Experiments on the reaction of Cl with pentane in CH_2Cl_2 and CCl_4 solutions have used transient electronic and vibrational spectroscopy to follow both the decay of the Cl radical reactant and the growth of the HCl product.[10] In that reaction, the rise time of the product and the decay time of the reactant are the same, consistent with simple sequential kinetics and in contrast to our observation for CN.[1] Other experiments on reactions of Cl use transient electronic absorption alone to determine the reaction rates of Cl with 16 different solutes in CH_2Cl_2 solution.[9]

Here we study the same solutes to make a direct comparison between the CN and Cl radical reactions. Because two complexes are important in the reactions of CN with solvent molecules,[1] we must consider both of them in analyzing reactions with added solute. We first observe both the decay of CN absorption and the growth of HCN absorption in the reaction of CN with pentane in CH_2Cl_2 and $CHCl_3$ solutions in order to develop and test our kinetic model. With the resulting analysis methodology in hand, we then extract the reaction rate constants for the 16 different solutes from the decay of the CN transient electronic absorption. These data allow us to compare the rates for reactions of CN and Cl with the different solutes as well as to assess the change in the rate with chlorine content of the solute. The dependence on Cl content that we observe for reactions of both CN and Cl apparently reflects systematic changes in the transition state with the chlorine atom content of the solute.

II. Experimental Approach

The experimental approach is essentially the same as we used previously,[1] and we only describe it briefly here. We photodissociate ICN with a pulse of 267-nm light to form CN radicals, and we monitor transient absorption at 400 nm using the B ← X electronic transition of the CN radical. We also observe the HCN reaction product with an infrared probe pulse near 3.07 μm in two systems. A Ti-sapphire oscillator and regenerative amplifier provide a 1-kHz train of 100-fs, 2.5-mJ pulses centered at 800 nm from which we generate the 267-nm photolysis light by frequency doubling the fundamental pulse and mixing the resulting 400-nm light with 800-nm light in β-barium borate (BBO) crystals. We use 0.75-μJ pulses of photolysis light in experiments detecting the CN reactant and 8-μJ pulses in experiments detecting the more weakly absorbing HCN product.

We monitor the 400-nm transient absorption either with light generated by frequency doubling the fundamental pulse in a BBO crystal (for the solvents CH_2Cl_2 and CH_3CCl_3) or with a continuum generated by focusing the fundamental pulse into a CaF_2 substrate (for the solvent $CHCl_3$). In the former case, we split the beam into a reference pulse, which we monitor to correct for laser power fluctuations, and a probe pulse, which passes through the sample. Each beam strikes an integrating silicon photodiode, and we average 1000 pulses at each step of the computer-controlled translation stage that determines the timing of the pulses. In the case of continuum probing, the reference and probe continuum pulses enter identical spectrometers and strike separate 512-element, 0.5-in. wide silicon photodiode arrays. We collect 300 pulses on the arrays, both with and without the pump pulse, and average 20 to 30 of these exposure pairs at each delay time.

Infrared light for HCN detection comes from a potassium niobate optical parametric amplifier. After separating the pulse into a probe and reference beam, we send the reference beam onto a lead selenide photodiode. The probe beam passes through the sample and into a 0.25-m monochromator with a 300-grooves/mm grating that disperses it onto a 32-element mercury cadmium telluride array. We average ten time traces, each of which contains 5000 pulses at each delay stage position. The relative polarization of the photolysis and probe pulses is 54.7° for all measurements in order to suppress the effects of rotational anisotropy. We measure the time resolution to be 1 ps and establish the timing of the photolysis and probe pulses using the coherent response generated when the 267-nm photolysis and 400-nm probe pulses are coincident in neat CH_2Cl_2. To minimize the effects of multiphoton signals that might arise for the more intense excitation pulse in the infrared absorption experiments, we reduce the peak energy by stretching the pulse to 3.25 ps. In addition, we subtract the background signal at the edge of the array, where there is no transient signal, and we do not fit the signal at delay times less than 50 ps.[1]

A Teflon gear pump circulates the sample through a 1-mm thick flow cell with 2-mm thick UV-grade MgF_2 windows. We synthesize ICN using a procedure[1] that is similar to those of Bradforth[3] and of Keiding.[12] We use 99.9% CH_2Cl_2 from Mallinckrodt Chemicals, >99.9% $CHCl_3$ from Sigma-Aldrich, and 99% CH_3CCl_3 from Sigma-Aldrich. The purity of the solutes (pentane, hexane, heptane, cyclopentane, cyclohexane, and cycloheptane, methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol, cyclohexyl chloride, 1-chlorobutane, 2-chlorobutane, 1,2-dichlorobutane, and 1,4-dichlorobutane) is at least 98%, and most are 99% or higher.

III. Kinetic Model

The kinetic model we use to analyze the transient absorption builds on our analysis of the reaction of photolytically generated CN radicals with the solvent[1] by including reaction with added solute, as shown in Figure 1. The essential feature in the kinetics is the rapid formation of two different types of complexes, a linear complex formed with rate constant k^{f}_{lin} and a bridging complex formed with rate constant k^{f}_{br}. In this model, the complexes form quickly compared to any subsequent reactions, and the bridging complexes with the solvent are primarily responsible for the 400-nm transient absorption. The 3.07-μm transient absorption comes from the HCN formed by the reaction of these two complexes.

A. Reaction with the Solvent. Our previous measurements of the reaction with solvent show that the CN radical transient absorption disappears 2.5 to 12 times more slowly than the HCN product appears, depending on the solvent.[1] These two timescales arise from the different reactivities of the two, chemically distinct complexes. Simple electronic structure calculations show that an isolated CN−CH_2Cl_2 complex has two minima with the structures shown in Figure 1. In these rudimentary calculations,

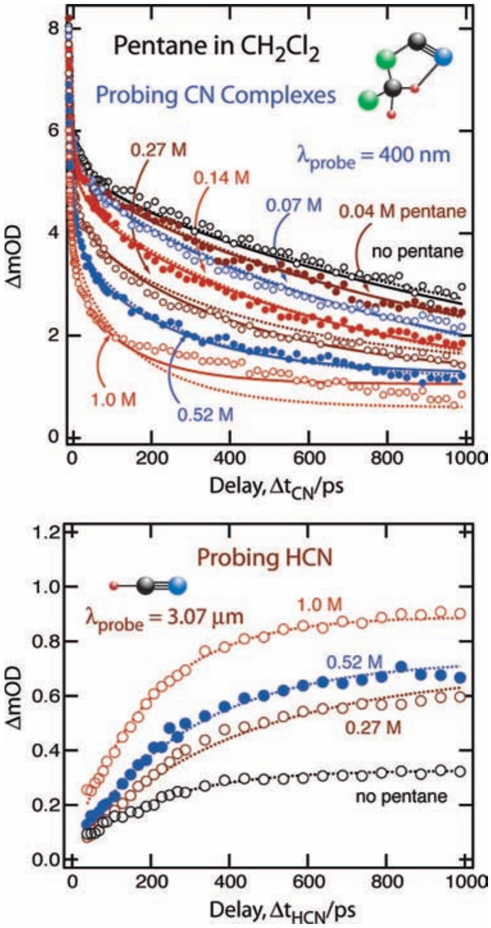

Figure 2. Top panel: Decay of the absorption at 400 nm in solutions of CN in CH_2Cl_2 with different concentrations of added pentane. The dashed curves are the simultaneous fits of the kinetic model (eqs 1 and 2) to the decay data and the growth data (bottom panel) as described in the text. The solid lines are fits of eq 1 to only the decays, using the parameters in Table 2. Bottom panel: Growth of the absorption at 3.07 μm in solutions of CN in CH_2Cl_2 with different concentrations of added pentane. The dashed curves are the simultaneous fits of the kinetic model (eqs 1 and 2) to these growth data and the decay data (top panel), using the parameters in Table 1.

the linear complex is bound by 430 cm^{-1}, and the bridging complex is bound by 1540 cm^{-1}.[1] Omitting the pathways shown by dashed arrows in Figure 1 reduces the kinetic scheme to the one that we have used to analyze the experiments on the solvent alone. That analysis shows that the bridging complex dominates the slow CN transient absorption and that the linear complex is the primary species reacting to form HCN. This behavior is consistent with the structures and binding energies of the complexes. The bridging complex is more abundant and less reactive because of its stronger binding, and the linear complex is less abundant but more reactive because of both its weaker binding and its favorable geometry for abstraction of an H atom from a solvent molecule. The calculations and fitting also suggest that the linear complex reacts with solvent to form either HCN or ClCN and that the bridging complex primarily reacts to form ClCN, as indicated in the figure.[1]

B. Reaction with Solute. The relative abundances and reactivities of these complexes is crucial to understanding CN reactions with added solute. We follow the reactions of the solutes by monitoring the transient absorption for different concentrations, as illustrated by the points in Figure 2 for the reaction of pentane with CN in CH_2Cl_2. As described below, we use only the decay of the CN transient absorption to extract rates for most of the solutes, but we use data for both the reactant decay and the product growth, as shown in Figure 2, to establish and test our analysis method. Including reaction of the complexes with the solute RH adds the two pathways denoted by the dashed arrows in Figure 1 to those for the reaction with the solvent. The added solute potentially reacts with either the linear or the bridging complex to form HCN (and for chlorinated solutes to form ClCN although we do not show that pathway explicitly). Because the tests described below show that reaction with the bridging complex is mostly responsible for the changes with added solute, we omit reaction of the linear complex with the solute from the present analysis.

One important aspect of experiments using a photolytic source of radicals is the extent to which the fragments recombine to reconstitute the precursor. As in our study of the reactions in neat solvents, we use the expression for diffusive geminate recombination[13,14] to account for that part of the early time evolution of CN. However, the differences in viscosity and complex stability for different solutes can alter the fraction of CN and I radicals that recombine in each solvent and for each solute concentration.

Assuming that the bridging complex is solely responsible for the transient electronic absorption in the kinetic scheme of Figure 1 and that both complexes react to produce HCN gives the transient absorption signals for CN-containing complexes $S^{(n)}_{CN}(t)$ and for the HCN products $S^{(n)}_{HCN}(t)$,

$$S^{(n)}_{CN}(t) = A_{CN}[1 - \phi^{(n)}\ \mathrm{erfc}(A/\sqrt{t})]\ \exp(-(k_{br} + k^2_{br,RH}C^{(n)}_{RH})t) + A^{(n)}_{offset} \quad (1)$$

$$S^{(n)}_{HCN}(t) = A_{HCN}(1 - \phi^{(n)})\left[\alpha[1 - \exp(-k_{lin}t)] + (1 - \alpha)\left(\frac{k^2_{br,RH}C^{(n)}_{RH}}{k_{br} + k^2_{br,RH}C^{(n)}_{RH}}\right)[1 - \exp(-(k_{br} + k^2_{br,RH}C^{(n)}_{RH})t)]\right] \quad (2)$$

The coefficients A_{CN} and A_{HCN} are arbitrary amplitudes, and A_{offset} accounts for a slowly decaying background that is essentially constant during the measurement.[15] The first term in brackets in eq 1 is the Smoluchowski expression for diffusive geminate recombination where ϕ is the fraction of radicals that recombine and A comes from the recombination time. In both equations, the pseudo-first-order rate constants for reaction of the bridging and linear complexes with the solvent, k_{br} and k_{lin}, come from fitting the data for reactions in the solvent alone.[1] The second-order rate constant for reaction of the bridging complex with the solute, $k^2_{br,RH}$, is one of the essential quantities we vary in the fitting the data for different solute concentrations, C_{RH}. In eq 2, the term $(1 - \phi)$ accounts for the varying number of CN radicals available to react at different solute concentrations, and $\alpha \equiv k^f_{lin}/(k^f_{lin} + k^f_{br})$ is the fraction of CN radicals that form linear complexes. The important competition in the reaction of the bridging complex is between formation of ClCN by reaction with the solvent and the formation of HCN by reaction with the solute. The term $k^2_{br,RH}C^{(n)}_{RH}/(k_{br} + k^2_{br,RH}C^{(n)}_{RH})$ accounts for the dependence of the branching between those two pathways on solute concentration. As described below, this term and the concentration dependence of the recombination fraction ϕ determine the variation of the asymptote of the HCN signal with solute concentration that is apparent in Figure 2. The quantities A, k_{lin}, and k_{br} are those obtained in our previous analysis of the transient absorption in the neat solvents,[1] and all variables with a superscript (n) can vary with solute concentration.

TABLE 1: Parameters for the Simultaneous Fits of the CN Decay and HCN Growth for the Pentane Solute

	fixed parameters				adjustable parameters		
solvent	A/ns$^{-1/2}$	k_{lin}/ns^{-1}	k_{br}/ns^{-1}	C_{RH}/M	ϕ_{max}	α	$k^2_{br,RH}$/ 10^9 M^{-1} s^{-1}
CH_2Cl_2	0.0065	4.8	0.67	0.03−1.0	0.89 ± 0.03	0.13 ± 0.02	4.9 ± 0.3
$CHCl_3$	0.0083	3.2	0.45	0.15−1.0	0.95 ± 0.03	0.11 ± 0.02	4.6 ± 0.3

TABLE 2: Parameters for the Fits of the CN Decay in the Solvent Alone and with Added Solute

solvent	A/ns$^{-1/2}$	ϕ	k_{br}/ns^{-1}
	no added solute		
CH_2Cl_2[a]	0.0065	0.818	0.67
$CHCl_3$[a]	0.0083	0.840	0.45
CH_3CCl_3[b]	0.0093	0.868	0.36 ± 0.10

solutes	C_{RH}/M	ϕ_{max}[c]	$k^2_{br,RH}$/10^9 M^{-1} s^{-1}
	CH_2Cl_2 solvent		
pentane	0.03−1.0	0.94	5.4 ± 2.0
hexane	0.20−1.6	0.96	3.3 ± 0.9
heptane	0.20−0.9	0.94	4.4 ± 0.5
cyclopentane	0.20−1.6	0.96	2.7 ± 0.9
cyclohexane	0.20−0.8	0.93	4.9 ± 1.9
cycloheptane	0.15−2.0	0.96	2.9 ± 0.4
methanol	0.15−0.6	0.88	4.4 ± 0.7
ethanol	0.15−0.6	0.88	5.6 ± 0.8
1-propanol	0.15−0.6	0.87	6.3 ± 0.8
2-propanol	0.15−0.6	0.88	5.8 ± 1.4
1-butanol	0.15−0.6	0.88	7.1 ± 1.3
cyclohexyl chloride	0.10−1.4	0.90	1.6 ± 0.8
1-chlorobutane	0.30−2.0	0.91	1.0 ± 0.3
2-chlorobutane	0.30−2.0	0.88	0.6 ± 0.5
1,2-dichlorobutane	0.30−2.0	0.84	0.4 ± 0.2
1,4-dichlorobutane	0.30−2.0	0.85	0.30 ± 0.25
	$CHCl_3$ solvent		
pentane	0.15−1.0	0.98	5.3 ± 1.5
heptane	0.20−0.8	0.96	4.4 ± 1.4
methanol	0.15−0.6	0.89	4.2 ± 1.1
1-chlorobutane	0.50−2.0	0.90	1.0 ± 0.5
2-chlorobutane	0.30−2.0	0.84	0.6 ± 0.2
	CH_3CCl_3 solvent		
heptane	0.20−0.8	0.99	2.0 ± 1.3
methanol	0.15−0.6	0.95	4.9 ± 0.7
1-chlorobutane	0.30−2.0	0.94	0.4 ± 0.2
2-chlorobutane	0.30−2.0	0.89	0.5 ± 0.1

[a] Reference 1. [b] These values come from fitting the neat solvent data to eq 1 with $C_{RH} = 0$ and a value of ϕ from scaling for the viscosity (ref 1). [c] The uncertainty in all of the values of ϕ_{max} is 0.03.

IV. Results and Discussion

The key observations in our experiments are the decays of the transient absorption of the complexed CN radical in reactions with 16 different solutes in solutions of CH_2Cl_2. For one solute, pentane, we also observe the growth of the transient absorption of the HCN product in two different solvents. This measurement is critical in identifying the roles of the two CN−solvent complexes in the reaction of the added solute and shows that reaction of the bridging complex with the solute is most important. That understanding informs our analysis of the decays we observe for alkane, alcohol, and chloroalkane solutes, and we are able extract second-order rate constants for the reaction of all of these solutes with the complexed CN radical.

A. Reactant Decay and HCN Product Formation in the Reaction of CN with Pentane. Figure 2 shows the decay of the transient electronic absorption of CN (top panel) and the growth of the transient vibrational absorption of HCN (bottom panel) for different concentrations of added pentane in CH_2Cl_2. One obvious qualitative feature is the increasingly rapid decay of the transient absorption of CN with increasing solute concentrations, behavior that is consistent with the reaction of CN radicals with pentane being substantially faster than their reaction with the CH_2Cl_2 solvent. The other qualitative feature is the change in the HCN transient absorption with increasing pentane concentration. The asymptote for the transient vibrational absorption in 0.27 M pentane is substantially larger than obtained with no added solute, and its magnitude increases further with the addition of more pentane. However, a 4-fold increase in pentane concentration to 1.0 M increases the asymptote by only about 50%. In addition, the rise time of the HCN transient absorption changes only modestly with increasing amounts of solute. These two observations suggest that reaction of the linear complex, which is the primary source of HCN in reactions with the solvent, is not responsible for most of the additional HCN we observe from reaction with the solute. If it were, the growth time would change substantially with added solute. The linear complex makes a relatively small contribution because it is present in low concentration, *not* because it reacts slowly with the solute. It is likely to react rapidly but have little influence on the rise in the presence of the larger contribution from the reaction of the bridging complex with the solute. To test this idea, we can fit the data to the restricted kinetic model illustrated in Figure 1.

We assume that the reaction of the linear complex with solute makes little difference in the growth of HCN, as indicated in Figure 1, and fit the data for CN and HCN transient absorption simultaneously to eqs 1 and 2. The dashed lines in Figure 2 are the fits generated by using the parameters in Table 1. The uncertainties for the adjustable parameters come from the diagonal elements of the covariance matrix for the fit. As described above, the parameters A, k_{lin}, and k_{br} come from our earlier analysis of the reaction of CN with just the solvent,[1] and the parameters ϕ, α, and $k^2_{br,RH}$ are the values that provide the best fit to the data. The fraction ϕ of the CN that recombines changes by as much as 15% over the full range of concentrations. Table 1 reports the maximum value ϕ_{max} for the largest solute concentration, and the Supporting Information gives the values of ϕ for each concentration. The best fit value of the fraction of linear complexes, α = 0.13, is consistent with our previous conclusion that the bridging complex is the dominant reacting species in solution.[1]

The most important parameter that we extract is the second-order rate constant for reaction of the bridging complex with added solute $k^2_{br,RH}$. As Table 1 shows, at the largest concentration of 1.0 M, the pseudo-first-order rate constant, $k_{br,RH} = k^2_{br,RH}C_{RH}$, is about seven times larger than the corresponding rate constant k_{br} for reaction with the solvent. The inherent reactivity of the bridging complex is much larger with the pentane solute than with the CH_2Cl_2 solvent. The second-order rate constant for reaction with solvent,[1] $k^2_{br} = k_{br}/C_{solvent} = (0.043 \pm 0.009) \times 10^9$ M^{-1} s^{-1}, is two orders of magnitude smaller than that with pentane, $k^2_{br,RH} = (4.9 \pm 0.3) \times 10^9$ M^{-1} s^{-1}. It is not surprising that the bridging complex reacts more rapidly with pentane than with the chlorinated solvents. We have shown that increasing chlorine content of the reaction partner decreases the reaction rate of CN with chloroalkanes[1] much as it does in both gas-phase[16−18] and condensed-phase[9] reactions of Cl.

The dashed lines in Figure 2 show that the kinetic scheme reproduces the data well except for the decay at the largest solute concentration. It reproduces both the strong dependence of the CN transient absorption on the concentration of added solute and the weak dependence of the HCN transient absorption on the concentration. However, the model neglects the reaction of the linear complex with the added solute, a process that almost certainly occurs, and it also leaves out hydrogen abstraction from the solvent by the bridging complex. The latter assumption is consistent with our analysis of the reactions of CN with the solvent alone. A more elaborate model incorporating these terms also fits the data well but produces uncertainties in the fitting parameters that exceed 100% because of correlation among the variables.[19] The fit to the decays of the CN transient absorption is better at the highest concentrations and the fit to the growth of the HCN transient absorption is worse for the pure solvent. Most important, however, is the value of the second-order rate constant for the bridging complex $k^2_{\mathrm{br,RH}}$, which is the same within the uncertainties given in Table 1. This analysis suggests that the reaction of the abundant bridging complex with pentane is fast enough to dominate the signal, overwhelming the contribution from the linear complex.

We have also applied this fitting strategy to the transient absorptions of CN and HCN in the reaction of CN with pentane in $CHCl_3$ solutions and obtained similar results, as shown in Table 1. The rate constants and branching fractions are nearly the same for the two solvents, and in both cases only the fit at the highest concentration fails to reproduce the data well. This difficulty arises in part from the constraint of fitting the growth of the HCN signal as well as the decay of the CN transient absorption. As discussed below, fits to decay data alone are satisfactory even at high concentrations. The poorer fits at the highest solute concentrations may reflect an additional, relatively slow reaction that is apparent only for the largest amounts of added solute. Our fits to the data for the reaction of CN with pentane in CH_2Cl_2 and $CHCl_3$ suggest that the decay of the 400-nm transient absorption reflects the reaction of the more abundant bridging CN−solvent complex and that the infrared transient absorption reflects the reaction of both the linear and bridging solvent complexes to form HCN.

B. Reactant Decay for Reaction of CN with Alkanes, Alcohols, and Chloroalkanes. Analyzing both the decay of the CN transient absorption and the growth of the HCN transient absorption provides a great deal of information about the reaction pathways, but the HCN absorptions are weak and difficult to measure. The analysis described above shows that we can fit only the decay of the CN transient absorption to eq 1 in order to extract the reaction rate of the bridging complex. The solid curves in Figure 2 show the quality of the fit to only the CN transient absorption data for added pentane solute. The fit is satisfactory, even at the highest concentration, although the less constrained fit gives larger uncertainties. The second-order rate constant, $k^2_{\mathrm{br,RH}} = (5.4 \pm 2.0) \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$, agrees with the value $(4.9 \pm 0.3) \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ obtained from simultaneously fitting the decay and growth of the HCN and CN transient absorptions.

Figure 3 shows similar fits to the decays for methanol (upper panel) and 1-chlorobutane (lower panel) in CH_2Cl_2 solutions, which are typical for all the solutes we study, and Table 2 gives the fitting parameters. The uncertainties come from adjusting the parameters until the quality of the fit deteriorates noticeably. The dark solid bars in Figure 4 are the second-order rate constants for reaction of CN with the 16 solutes in CH_2Cl_2 solution. The second-order rate constants for the alkanes are about $4 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$, and those for the alcohols are larger, increasing from $4 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ to $7 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ in going from methanol to 1-butanol. The reaction of CN with the chloroalkanes is markedly slower. The largest rate constant is only $1.6 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ for cyclohexyl chloride and decreases to $0.3 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ for 1,4-dichlorobutane. The value of the fraction ϕ that recombines increases slightly with added solute, as shown in the Supporting Information, and in all cases, the

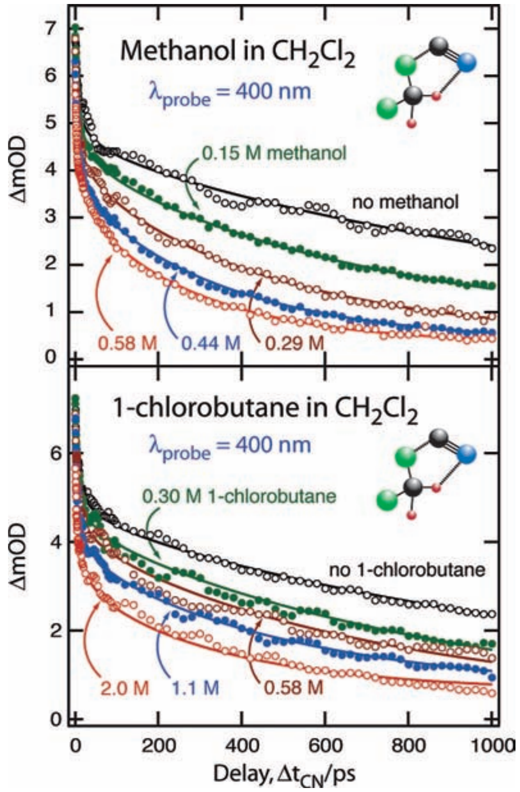

Figure 3. Top panel: Decay of the absorption at 400 nm in solutions of CN in CH_2Cl_2 with different concentrations of added methanol. The solid lines are fits of eq 1 to the data with the parameters given in Table 2. Bottom panel: Decay of the absorption at 400 nm in solutions of CN in CH_2Cl_2 with different concentrations of added 1-chlorobutane. The solid lines are fits of eq 1 to the data with the parameters given in Table 2.

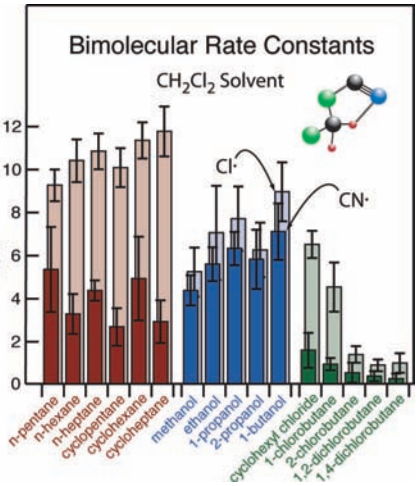

Figure 4. Second-order rate constants $k^2_{\mathrm{br,RH}}$ for reaction of CN radicals (dark bars) and Cl radicals (light bars) with various solutes in CH_2Cl_2 solvent.

maximum value is $\phi_{\max} = 0.85$ or larger. Thus, most of the initially formed CN recombines, but the fraction is noticeably larger ($\phi_{\max} \approx 0.95$) for the alkane solutes. The large amount of recombination in the alkanes may reflect their inability to complex the CN radical and prevent its recombination compared to the alcohols and chloroalkanes.

The 16 solutes we study in CH_2Cl_2 are the same ones whose reactions with Cl we studied earlier,[9] and the interpretation of those earlier results for Cl provides a context for understanding the CN data. The reaction rate with Cl decreases in going from the alkanes to the alcohols to the chloroalkanes,[9] as shown by the lightly shaded bars in Figure 4. The very weakly bound complex[9,20] that reacts in the case of Cl and the bridging complex that reacts in the case of CN have important differences. The bridging complex is more strongly bound and has interactions with both ends of the CN radical. The stronger binding can increase the activation energy for the reaction of the CN complex compared to the Cl complex, and the simultaneous binding of the carbon (to a chlorine) and the nitrogen (to a hydrogen) in the bridging complex can impose more severe steric restrictions on the reaction with added solute. In agreement with this qualitative picture, the alkane solutes react a factor of 2 to 3 more slowly with CN in the bridging complex than with Cl in its weaker complex. The same trend holds for the chloroalkanes, which react several times more slowly with CN than with Cl. As the chlorine content of the solute increases, the reaction rate for the CN bridging complex decreases, reflecting the deactivating effect of chlorine substituents that we have also observed in reaction of linear and bridging CN complexes with several chlorinated solvents.[1] This reduction of the reactivity with increasing chlorine substitution is consistent with the behavior observed in reactions of Cl in both liquids[9] and gases.[16−18]

The reactions of Cl and CN with alcohols do not show the same trend as those with the alkanes and chloroalkanes. As Figure 4 illustrates, the rate constants for the alcohols are nearly the same for both reactants, unlike the situation for the other solutes. The stronger interactions that the alcohols can have with both CN and its ICN precursor may be responsible for this similarity. The complexes of CN radicals with water and alcohols are relatively strong, as shown by electronic structure calculations that obtain a binding energy of about 600 cm^{-1} for the CN−H_2O complex.[21] If their strength were intermediate between that of the bridging and linear complexes, they could be more abundant than the linear complex but more reactive than the bridging complex. Thus, some of the CN radicals destined to form bridging complexes might form more reactive complexes with the alcohol solute. Alcohols could also preferentially solvate the ICN precursor, placing the CN adjacent to an alcohol molecule with which it reacts after photolysis. Ultrafast measurements that find methanol and ethanol oligomers in carbon tetrachloride are consistent with this possibility.[22−24] They suggest that at our solute concentrations, the alcohol oligomers contain three or four molecules and are large enough to solvate an ICN molecule effectively.[22] Because the maximum alcohol concentration of 0.6 M in our experiments is a factor of 6 larger than the ICN concentration, there are enough alcohol molecules to solvate the ICN.

The results described above address the trends in reactivity with the identity of the reacting solute, but we can also determine the sensitivity of the reaction rate for CN to the identity of the solvent. We have applied the same analysis to transient absorption data for representative solutes in $CHCl_3$ and CH_3CCl_3. Figure 5, which compares the second-order rate constants for the reactions in three solvents, shows that there is no substantial variation among them with the possible exception of the reaction of *n*-heptane. The similarity in the reaction rates suggests that the bridging complexes have similar stabilities and, likely, conformations in these three solvents. Although the solvent CH_3CCl_3 is potentially different because it cannot form the analogous bridging complex across a single carbon atom, the reactivity is the same. It is likely that complexation occurs across two carbon atoms to form a complex with a Cl−C−N angle similar to that in the complexes of CN with CH_2Cl_2 and $CHCl_3$.

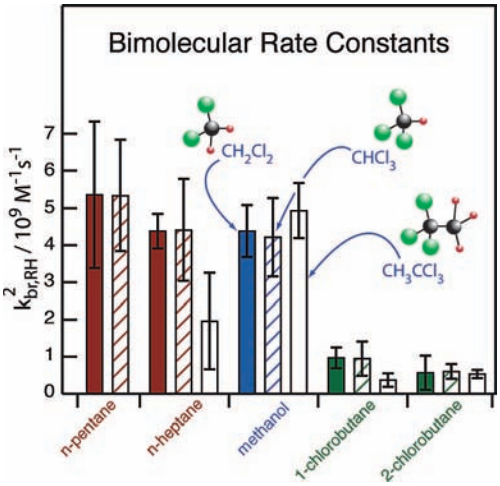

Figure 5. Second-order rate constants $k^2_{br,RH}$ for reaction of CN radicals with selected solutes in CH_2Cl_2 (solid bars), $CHCl_3$ (hatched bars), and CH_3CCl_3 (open bars) solutions.

V. Summary

Time-resolved experiments examining CN radical reaction rates with 16 different alkane, alcohol, and chloroalkane solutes in CH_2Cl_2 and with a smaller number in $CHCl_3$ and CH_3CCl_3 identify the roles of complexes in reactions of CN in solution. The experiments generate CN radicals by 267-nm photolysis of ICN and monitor the transient electronic absorption of the CN radical or the transient vibrational absorption of the HCN products. The key to understanding the transient absorption is the presence of both linear and bridging complexes of the CN radical with solvent molecules.[1] Studying both the growth of the HCN absorption and the decay of the CN absorption in the presence of a pentane solute shows that reaction of the bridging complex with the added solute is the primary source of the additional HCN. With this understanding in hand, we analyze the decay of the transient absorption of CN in reactions with a set of alkane, alcohol, and chloroalkane solutes in CH_2Cl_2 for comparison with a previous study on the reactions of the same solutes with Cl.[9] The slower reactions of CN in the bridging complex with the alkanes and chloroalkanes compared to reactions of Cl likely reflect the stronger binding of the CN−solvent complex and additional steric effects. However, the rates for CN and Cl are essentially identical for the alcohol solutes. The similarity for the alcohols may reflect the formation of a relatively strong, reactive CN−alcohol complex and the preferential solvation of ICN by the alcohols. We also observe the reactivity of the CN bridging complex for five of the solutes in CH_2Cl_2, $CHCl_3$, and CH_3CCl_3 and find that solvent has little effect on the reactivity, suggesting that the bridging complexes have similar stabilities and conformations in these three solvents.

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Supporting Information Available: Tables of the best-fit recombination fraction ϕ for each concentration of added solute. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The parameters A_{CN} and A_{HCN} reflect both the absorption probability and concentrations of the species. In our study of the reaction with the solvent, ref 1, we used these parameters to estimate concentrations. However, the uncertainty in extinction coefficients results in a larger range of possible values. Thus, we do not attempt to extract that information here. The offset, A_{offset}, apparently arises from solvent radicals formed in the reaction with CN. This conclusion is consistent with our observation that at a delay of 9 ns the offset is smaller for more concentrated solutions, in which there are fewer solvent molecules.

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