mation. At higher ketone concentrations, the solution is more polar and would favor the formation of an ionic complex. An ionic nature is also suggested by the water solubility and by the large entropy change. Large entropy changes usually occur during formation of ionic compounds in solvents which are not highly polar.

While the iodine molecules in Figure 6 are drawn to suggest bonding to the lone-pair electrons of the keto oxygen, it is likely that π-electron bonding is also involved. Other structures could be drawn with the dimer complex in the enol form. There are, in fact, a fairly large number of structures possible. Certainly there are enough possibilities to make plausible the assumption of dimer and even polymer charge-transfer complex formation.

The Photoproduction and Recombination of Bromine Atoms in the Liquid Phase

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Contribution from the Institute of Physical Chemistry, University of Uppsala, Uppsala, Sweden. Received April 15, 1965

The photoproduction and recombination of bromine atoms in carbon tetrachloride has been studied at room temperature by flash spectrophotometric techniques. The primary quantum yield of dissociation ($\phi = 0.22$) is ca. 100 times as great as that deduced previously by indirect means, but is only slightly greater than that for iodine under comparable conditions, in agreement with the assumption that the solvent behaves as a continuous medium. The second-order rate constant is $k = 1 \times 10^{10}$ l. mole^{-1} sec.$^{-1}$, where $d[\mathit{I}]/dt = 2\phi I_a - 2k[\mathit{I}]^2$, in correspondence with a diffusion-controlled recombination process involving small diffusive displacements.

Introduction

The primary quantum yields of photoproduction and rates of recombination of iodine atoms in inert solvents have been determined by several techniques, including flash photolysis[2-4] and a combined rotating sector[5]–steady-state illumination,[6] or rotating sector–allyl iodide atom scavenger method.[7,8] Results obtained by the various methods are in quite satisfactory agreement and have been used in combination with photochemical space intermittency effect results to measure iodine atom diffusion coefficients[9,9a] and to develop a theory of solution photodissociation based on the solvent as a continuous medium.[10]

The primary quantum yield of photodissociation of molecular bromine in carbon tetrachloride has been deduced indirectly from a comparison of the thermal and photochemical exchange reactions between bromine and bromotrichloromethane.[11] Assuming the same reaction mechanisms and rate constants (except for the initial step), and that the constant for the equilibrium between bromine atoms and bromine molecules is the same in the gas and liquid phases, the quantum yield equals 0.0025 at 50°. This result is surprisingly low in comparison to that for iodine (0.14 at 25° 0.21 at 38°[7]), as theoretically the primary quantum yield for bromine should be somewhat *greater* as a result of the smaller atomic diameter and the greater excess energy (following dissociation) of the bromine atoms.

In attempting to determine the recombination of bromine atoms in carbon tetrachloride by measuring the decrease in steady-state molecular concentration upon illumination by a relatively strong continuous light source, Rabinowitch and Wood actually observed a very small *increase* in absorption in the visible region.[6,12] A similar but stronger effect was observed for iodine in benzene, methanol, and water, and in the case of benzene was attributed either to the destruction of a benzene–iodine complex by light or to the formation during illumination of a new complex involving iodine atoms.[12] More recent studies of iodine–benzene solutions by flash techniques have shown the same increase in absorption[13,14] and have led to the conclusion that a charge-transfer complex is formed between the benzene molecule (donor) and iodine atom (acceptor) species. Although carbon tetrachloride does serve as an acceptor in some charge-transfer interactions,[15] the complexes are in general quite weak, and it is very doubtful that the increased absorption ob-

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served by Rabinowitch and Wood is interpretable in terms of formation of a carbon tetrachloride–bromine atom charge-transfer complex.

The molecular extinction coefficient for bromine is smaller (by approximately a factor of five) than that for iodine, and therefore the direct measurement by the flash photolysis technique of the primary quantum yield and recombination (being second order) of bromine atoms is considerably more difficult. Required is a flash apparatus capable of producing a very short but very high intensity flash, and a kinetic spectrophotometer capable of measuring very small changes in absorbance. The work reported here was undertaken with a high-voltage flash apparatus designed at this Institute, utilizing components and techniques especially to reduce self-inductance, underdamping, and flash intensity tailing to a minimum, consistent with high-peak intensity output.

Experimental

Apparatus. The flash photolysis apparatus used in this work (Apparatus V at the Institute) has been described previously.[16] The maximum energy that can be discharged with this unit is 8000 joules (50 kv., 6.4 μf.). It has been shown, however, that the peak light intensity (of primary importance for very fast reactions, rather than total flash light output) is not a linear function of the electrical energy discharged above *ca.* 1500 joules, but it appears to reach a constant value resulting in longer flash duration times as the discharge energy is increased.[16] Also, the electrical discharge circuit is slightly underdamped, as shown by a shoulder on the flash profile curve (Figure 4, ref. 16), which also results in longer flash duration times. The optimum conditions under which to study the reaction reported here were found to be with a 0.15-ohm carbon damping resistor in series with the two flash lamps in the discharge circuit operated at 30 kv. (6.4 μf., 2880 joules); although 54% of the energy is dissipated across the carbon resistor, the peak intensity is reduced only about 10%, and the decay of the light intensity from its maximum at 3 μsec. is closely exponential (with a half-life of 4.5 μsec.) to 35 μsec., where the intensity has decreased to less than 1% of its peak value.

The flash kinetic spectrophotometer has been described in detail.[17] The continuous analyzing light from an Osram Type XBO 450 xenon lamp (supplied by a d.c. generator) was collimated through the cylindrical Pyrex reaction cell (30-mm. i.d., 200-mm. light path), focused on the entrance slit of a Zeiss MM12 double monochromator with glass prisms, and detected by an E.M.I. 9552A photomultiplier tube. Transient changes in transmittancy following the flash were displayed on a Tektronix Type 565 double-beam oscilloscope with Type 3A1 plug-in units (the response time of the apparatus thus being limited by the oscilloscope to *ca.* 1 μsec.) and photographically recorded. All measurements on the bromine–carbon tetrachloride systems were made at 420 mμ with a slit width of 1 mm. (3-mμ band width). Calibration traces corresponding to a 1% change in transmittancy between them were recorded immediately after each flash by decreasing the

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oscilloscope sensitivity a factor of 100 and photographing by double exposure the d.c. output with and without the analyzing beam on.

Materials. The extent and adequacy of the solvent purification procedure were determined by the required elimination of any permanent change in bromine concentration, either after repeated flashings or continuous illumination. Chlorine was added to carbon tetrachloride (Merck "pro analyzi" or Hopkin and Williams "Spectroscope") and the solution was illuminated with a 200-w. tungsten lamp for a period of from 2 to 6 days until no further photochlorination occurred, chlorine being added as it was used up. Excess chlorine was removed by washing with sodium sulfite solution. The wet carbon tetrachloride was stirred for 3 hr. with concentrated sulfuric acid, washed, stirred for 3 hr. with concentrated sodium hydroxide, washed, and distilled twice over phosphorus pentoxide through a 40-cm. Vigreux column, the final distillation at a high reflux ratio and only the middle fraction being retained.

Bromine (Merck guaranteed reagent) was used without further purification, except that one distillation resulted when each solution was prepared by allowing the vapor from liquid bromine to dissolve in the carbon tetrachloride. The bromine concentration in the cell was determined spectrophotometrically with the continuous analyzing beam and detector of the flash apparatus by comparing the absorbances relative to air for pure carbon tetrachloride and the bromine solution (assuming ϵ 208 l. mole^{-1} cm.$^{-1}$ at 420 mμ).

Results

Rate of Recombination. Typical oscillograms are shown respectively in Figures 1a and 1b for scattered light (analyzing light off) and transient absorbance changes following the flash, a deflection in the negative direction corresponding to a decrease in absorbance. The lower trace in each oscillogram, at one-tenth the sweep time of the upper trace, was used to indicate the extent of any irreversible photobromination occurring as a result of solvent impurities. (The apparent slow decrease in absorbance after the lower trace of Figure 1b had returned to the base line resulted from a 1% a.c. component in the current from the generator power supply for the xenon analyzing lamp; the frequency of this ripple was low enough so that it affected only the ability to keep the oscilloscope trace on screen and not the accuracy of the kinetic data.) In general at least five scattered light traces were averaged to correct the deflections observed with the analyzing light on. The extensive shot noise on the oscillograms with the analyzing light on is a consequence of having to measure very small changes in transmittancy (less than 1%) in times less than 200 μsec.; further reduction in the shot noise by filtering led to distortion of the transmittancy signal.

Figure 2 shows a plot of the reciprocal of the change in absorbance, ΔA, as a function of time for the oscillogram in Figure 1b after correction for scattered light. The expected second-order recombination is clearly indicated by this linear behavior over a change by a factor of six in bromine atom concentration ([Br] $= -\Delta A/2\epsilon_{Br_2}d$, where ϵ_{Br_2} is the molar estinction coefficient for molecular bromine and d is the light path
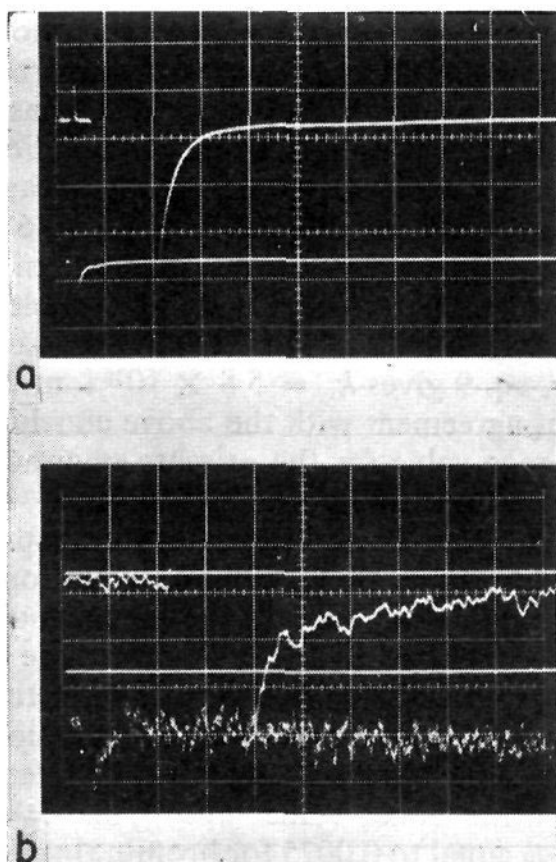
Figure 1. Oscillograms of the recombination of bromine atoms in carbon tetrachloride. Analyzing wave length = 420 mμ, [Br₂] = 3.5 × 10⁻⁵ M. Sweep times: upper trace, 20 μsec. per major vertical division; lower trace, 200 μsec. per major vertical division. (a) Analyzing light off, showing the flash light scattered by the reaction cell. (b) Xenon analyzing light on; the separation between the two straight horizontal traces corresponds to 1% change in transmittancy.
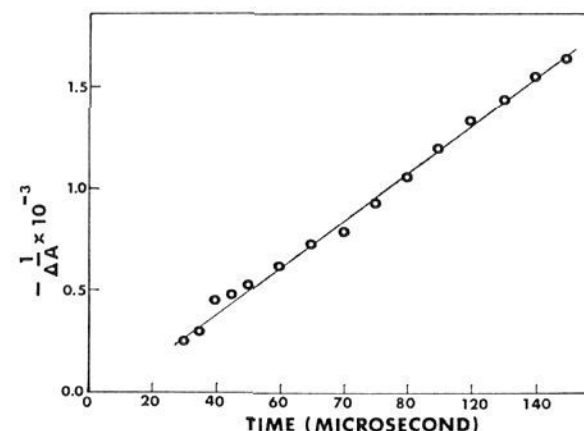

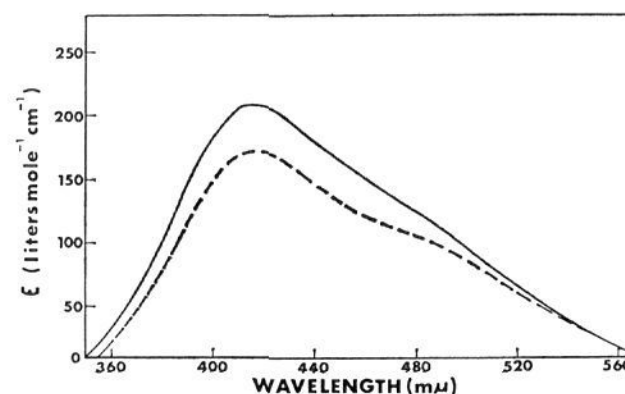Figure 2. Second-order plot for oscillogram in Figure 1b corrected for scattered light in Figure 1a.

Figure 3. Comparison of visible absorption curves for bromine in carbon tetrachloride solution (solid line) and in the gas phase (dashed line).

of the reaction cell). The recombination rate constant, k, defined by the rate law

$$-\frac{d[\text{Br}]}{dt} = 2k[\text{Br}]^2 \tag{1}$$

was calculated from the slope of the second-order plot for each of at least ten oscillograms taken for each cell. These results for eight cells are summarized in the penultimate column of Table I.

Table I. Summary of Results for the Room Temperature Recombination of Bromine Atoms in Carbon Tetrachloride

Concn., M		k, l.	ϕ
$[\text{Br}_2]_0$	$[\text{Br}]_{40\mu\text{sec}}$	mole⁻¹ sec.⁻¹	
3.5 × 10⁻⁵	1.11 × 10⁻⁶	1.13 × 10¹⁰	0.21
5.3	1.59	0.91	0.27
5.4	1.30	1.14	0.23
8.4	1.60	0.99	0.21
8.8	1.38	1.14	0.17
9.2	1.93	0.89	0.30
11.0	1.42	1.09	0.14
13.4	1.91	0.95	0.24
		Average 1.0 (±0.1) × 10¹⁰	0.22 (±0.04)

Primary Quantum Yield. The complete expression for the rate of production and recombination of bromine atoms is

$$\frac{d[\text{Br}]}{dt} = 2\phi I_a - 2k[\text{Br}]^2 \tag{2}$$

The light absorbed, I_a, is a function of time but is directly proportional to the light profile of the flash lamp (Figures 4b and 5, ref. 16) provided only a small

fraction of the molecular bromine is dissociated at any given time during the flash.

A convenient actinometer for flash studies involving halogens in solution is the measurement with identical cells and positioning of the extent of dissociation of the same halogen in the gas phase, the gas-phase quantum yield of dissociation being unity at reasonable inert gas pressures. This obviates the necessity of knowing accurately the spectral distribution of the flash light, provided the absorption spectra in the two phases are equal or proportional, since for small absorption[3]

$$(I_a)_{\text{soln}} = (I_a)_{\text{gas}} \frac{[\text{X}_2]_{\text{soln}} \, \Sigma(I_0)_\lambda(\epsilon_{\text{soln}})_\lambda}{[\text{X}_2]_{\text{gas}} \, \Sigma(I_0)_\lambda(\epsilon_{\text{gas}})_\lambda} \tag{3}$$

where $[\text{X}_2]$ is the halogen concentration, and I_0 is the incident light intensity (in quanta per unit area per second). The visible absorption curves for bromine in carbon tetrachloride and the gas phase are compared in Figure 3, showing that, while the above proportional condition is not strictly true at all wave lengths, the neglect of wave length variations in the incident light intensity is reasonable. From Figure 3, $\Sigma(\epsilon_{\text{soln}})_\lambda/\Sigma(\epsilon_{\text{gas}})_\lambda = 1.20$, so that

$$(I_a)_{\text{soln}} = 1.20[\text{Br}_2]_{\text{soln}} \left(\frac{(I_a)_{\text{gas}}}{[\text{Br}_2]_{\text{gas}}}\right) \tag{4}$$

Values of the ratio $(I_a)_{\text{gas}}/[\text{Br}_2]_{\text{gas}}$ were obtained as a function of time for three bromine–argon cells ([Br₂]/[Ar] ratios from 0.015 to 0.031) by digital integration of eq. 2 using the Runge–Kutta method, the integration being carried out at 0.5-μsec. intervals from 0 to 40 μsec. to give the measured value of the bromine atom concentration at 40 μsec. with the experimentally determined apparent second-order rate constant $k_{\text{app}} = k[\text{Ar}]$. The average curve (with a deviation of less

than $\pm 4\%$) was used to calculate $(I_a)_{soln}$ from eq. 4 for solution cells of the eight different bromine concentrations tabulated in the first column of Table I; eq. 2 was then solved for ϕ by machine integration as above using the average value of k for each cell, the results being given in the last column of Table I.

Discussion

The average observed rate of recombination from Table I, 10^{10} l. mole^{-1} sec.$^{-1}$, is in only fair agreement with that calculated for the diffusion-controlled recombination assuming that even on a molecular scale the solvent can be treated as a continuous medium of viscosity η. If the encounter diameter in solution ($2a$) pertinent to the recombination process is considered equal to the diffusion diameter ($2a_s$) of the atomic species, combination of the Smoluchowski relation for identical particles

$$k = \frac{8\pi a D N}{1000} \text{ (l. mole}^{-1}\text{sec.}^{-1}) \tag{5}$$

and the Stokes–Einstein equation for the atomic diffusion coefficient

$$D = \frac{kT}{6\pi\eta a_s} \text{ (cm.}^2\text{ sec.}^{-1}) \tag{6}$$

leads to an expression for the diffusion controlled rate of recombination that is independent of the properties of the reacting species.

$$k = \frac{4NkT}{3000\eta} \tag{7}$$

At 25°, $k = 0.35 \times 10^{10}$ l. mole^{-1} sec.$^{-1}$ for recombination in carbon tetrachloride.

The assumptions involved in the derivation of eq. 7, however, make it inadequate for application to atom recombination for several reasons. Equation 6 is based on the condition that the diffusing species are large compared to the solvent molecules and predicts a diffusion coefficient for iodine atoms too low by a factor of ca. four (i.e., 1.1×10^{-5} as compared to the recently determined[9] value for D_I of 4×10^{-5} cm.^{2} sec.$^{-1}$). For solvent and solute molecules of comparable size a more thorough treatment[18] gives

$$D = \frac{kT}{\sigma\eta} \tag{8}$$

where σ is the mean diffusive displacement between successive equilibrium positions. (That σ is considerably less than $6\pi a_s$ is also concluded from the magnitude of the primary quantum yield of dissociation in solution, ϕ (discussed below), although admittedly this conclusion also develops from treating the solvent as a continuous medium.) Further, it has been pointed out by Noyes[19] that the use of a more realistic boundary condition (i.e., that the diffusing species have a finite average concentration at the separation of centers occurring at recombination) leads to the more general expression

$$k = \frac{8\pi a D N/1000}{1 + 8\pi a D N/1000 k_c} \tag{9}$$

where k_c would be the rate of recombination with an equilibrium distribution of atoms unperturbed by the recombination reaction. In general k_c has been assumed to be the collision frequency in solution[20] which is presumed to be equal to (or slightly greater than[21]) the gas-phase collision frequency (i.e., ca. 6×10^{10} l. mole^{-1} sec.$^{-1}$ for halogen atoms at room temperature). Using the measured value for k from Table I (10^{10} l. mole^{-1} sec.$^{-1}$), $a = 2 \times 10^{-8}$ cm., and assuming that $D_{Br} = D_I$, eq. 9 gives $k_c = 5.8 \times 10^{10}$ l. mole^{-1} sec.$^{-1}$, in excellent agreement with the above conclusion.

The average value for the primary quantum yield of photodissociation of molecular bromine in carbon tetrachloride from Table I indicates that approximately 22% of the bromine atoms from flash photoproduction escape recombination back to the parent molecule in a time short compared to the resolution time of the detecting apparatus. This is comparable to the value of ca. 0.14 for the primary quantum yield of iodine atom production in the same solvent[2,3,7] at room temperature.

On the other hand, Miller and Willard[11] indirectly calculated ϕ equal to 0.0025 for bromine in carbon tetrachloride at 50°. This determination was based on a comparison of the thermal and photochemical exchange reactions between bromine and bromotrichloromethane, and involved the assumption that the mechanisms for the two processes were the same at 50° except for the initial dissociating steps. The thermal data also had to be extrapolated from 135 to 50°, the rate of recombination for bromine atoms in solution was chosen to be the collision frequency in the gas phase, and the constant for the equilibrium between molecular and atomic bromine was assumed to be the same in the gas phase and in carbon tetrachloride. The uncertainties associated with these latter assumptions are not adequate to account for the approximately 100-fold difference between the quantum yield obtained in this work and the calculated value of Miller and Willard, and it is implied that the thermal and photochemical exchange processes are not comparable in this manner at 50°.

Noyes[10] has developed a rather straightforward treatment of the photodissociation of diatoms based on the solvent as a continuous viscous medium, so that the probability (β_0) that two particles whose centers are initially separated by photolysis to a distance r_0 will eventually encounter each other (and hence recombine) is determined solely by random walk. For reasonably large values of r_0 compared to the mean diffusive displacement σ, $\beta_0 = 2a\beta/r_0$, where β is the probability that two species separating from a nonreactive encounter will eventually encounter each other at least once more.[22]

The initial separation r_0 is assumed to result from the excess kinetic energy of the atoms following photoproduction, so that[22]

$$r_0 = 2a + \frac{[m(h\nu - \epsilon)]^{1/2}}{3\pi\eta a} \tag{10}$$

where $h\nu$ is the energy of light absorbed, and ϵ is the dissociation energy of molecular bromine (45.5 kcal. mole^{-1}). Assuming an average wave length of 440 mμ

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for the unfiltered flash light gives $r_0 = 4.8 \times 10^{-8}$ cm., hence $\beta_0 = 1 - \phi = 5\beta/6$ and $\beta = 0.935$. It can be shown[23] further that $\sigma \cong [3a(1 - \beta)]/\beta$ for small values of σ, and therefore the mean diffusive displacement is ca. 0.4×10^{-8} cm. based on the above value for β.

The assumption that the liquid is a continuous medium is obviously quite severe in view of such a small calculated diffusive displacement. Required is that the diffusive process take place by a series of very small steps occurring at very high frequency and hence low activation energy. This is consistent with the constant-volume measurements on the diffusion of molecular iodine in carbon tetrachloride[24] and the self-diffusion of carbon tetrachloride,[25] whereby the temperature coefficients of diffusion are very nearly the temperature coefficient of kinetic energy. However, in view of the discrepancies between the measured and calculated parameters in the diffusion-controlled rate expression, Noyes[20] has concluded that a small but significant energy barrier exists for recombination and dissociation processes.

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Electron Spin Relaxation in Pseudo-Tetrahedral Cobalt(II) and Nickel(II) Complexes in Solution[1a]

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It is shown that the well-resolved proton magnetic resonance spectra of the paramagnetic, pseudo-tetrahedral Ni(II) complexes with aminotroponeimines and salicylaldimines, and the Ni(II) and Co(II) complexes with triarylphosphines, are the result of very short electron relaxation times, of magnitude $\sim 10^{-13}$ sec. The possible mechanisms responsible for these short relaxation times are investigated, and it is concluded that: (1) dynamic interconversion between diamagnetic and paramagnetic forms in solution for the Ni(II) complexes is too slow to be the dominant relaxation mechanism; (2) coupling of the zero field splitting to the tumbling of the complex in solution dominates the relaxation time for both the Co and Ni systems of interest. For the Ni complexes, these conclusions are reached by systematic elimination of the other possible mechanisms and by demonstrating that the electronic structures for these complexes favor the appearance of large zero field splittings necessary for such rapid relaxation. For the Co complexes, it is demonstrated that the short relaxation times can be quantitatively accounted for by a zero field splitting constant well within the range of values observed for other tetrahedral Co systems. The differences in p.m.r. line width for some triarylphosphine and aminotroponeimine complexes in carbon disulfide and chloroform are shown to be consistent with this relaxation mechanism.

Introduction

The appearance of a well-resolved proton magnetic resonance (p.m.r.) signal for paramagnetic complexes is the result[2] of their unpaired electron(s) possessing a very short relaxation time, T_1, or exchange time, T_e. For a sufficiently short electronic relaxation time, the p.m.r. line width for the complex may be only imperceptibly broader than for the diamagnetic ligands.[3]

Recently, a number of paramagnetic systems containing tetrahedrally coordinated Ni(II)[4-6] and Co(II)[7] have been investigated, whose p.m.r. spectra are characterized[4,8-14] by very narrow line widths (as narrow as 4–5

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