can the reaction

$$O^- + O^- \longrightarrow O_2^{2-} \tag{23}$$

account for the decay because k_{23}, under our conditions, would be required to be $>10^{12}\ M^{-1}\ \text{sec}^{-1}$ as calculated from the data of Felix, *et al.*[7] The reaction may, however, be

$$O_3^- + O^- \longrightarrow O_4^{2-} \tag{24}$$

for which we estimate $k_{24} \approx 5 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ using the sequence of reactions 2, 5, 20, and 24 and the steady-state approximation for $[O^-]$ to determine the decay equation for O_3^-.

Acknowledgment. We are indebted to Dr. Gideon Czapski with whom this work was frequently discussed, and with whose group we have had an effective exchange of information. Mr. E. G. Wendell was responsible for the successful operation of the Linac and of the detection equipment.

Brønsted Catalysis of the Fading Reaction of Flash-Produced Transients from 2,6-Dinitrotoluene

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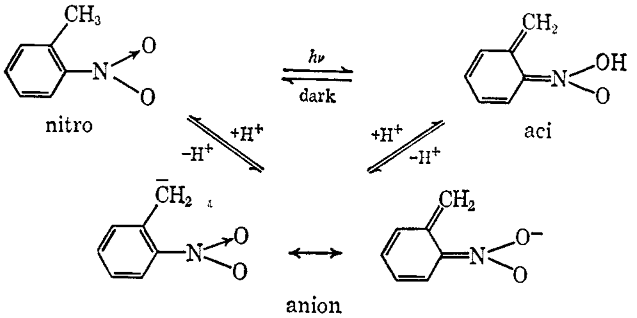
Contribution from the Pioneering Research Laboratory, U. S. Army Natick Laboratories, Natick, Massachusetts 01760. Received October 17, 1968

Abstract: 2,6-Dinitrobenzyl anion, $\lambda_{\max}$ 500 mμ, was produced by flash photolysis of 2,6-dinitrotoluene. A study of the catalysis of the reaction, 2,6-dinitrobenzyl anion + HA → 2,6-dinitrotoluene, with acids whose pK's vary from −1.75 to 16.75 has shown that the Brønsted α varies from 0 to 1 as the pK of the donor is increased. The limiting rate of proton transfer in this system (where $\alpha = 0$) is around 10^5 l. mole^{-1} sec^{-1} at 30°, far below diffusion control. Other factors such as H bonding between anion and donor acid and charge delocalization in the anion must be responsible for the relatively slow proton transfer to carbon. The Arrhenius activation energy for protonation of the anion by H_2O is 11.5 kcal mole^{-1}. The transient produced by flashing acid solutions had a $\lambda_{\max}$ of 410 mμ and is the *aci* form of 2,6-dinitrotoluene. Its pK_a was determined to be 1.8. The direct tautomerizm of *aci* to nitro form has a rate of 2×10^3 sec^{-1} at 30° and an Arrhenius activation energy of 10.1 kcal mole^{-1}.

A number of careful studies of the general acid catalysis of nitrobenzyl anions produced from aromatic nitro compounds having alkyl substituents have been made in recent years. In the majority of these studies, the anion was produced by reaction with strong ethoxide in alcoholic solvent and the catalysis of the return reaction studied at low temperature by addition of excess catalyzing acid.[1–4]

It has been shown that similar anions may be produced photochemically by decarboxylation of the corresponding nitrophenylacetate ion,[5] or by ionization of the initial photoproduct from flash photolysis of *o*-nitrotoluenes. In the latter case the initial photoproducts appear to be the *aci*-nitro species which, because of the low pK_a, are ionized completely to anion in aqueous solutions of pH greater than 2 or 3.[6–8] The latter method offers some advantages for catalysis studies. First, aqueous solutions in which acidity is easily defined are used. This is an advantage since the kinetic constants are ultimately related to the thermodynamic pK's of the catalyzing acids. Second, since flash methods produce the anion homogeneously dispersed in an equilibrated system, rate measurements are not limited by speed of mixing and can be made at room temperature using fast oscilloscope recording methods. Third, the catalysis can be studied over a very wide range of pH since the production of anion does not depend on a high initial pH as in photolysis of the carboxylate ion or direct ionization by ethoxide.



Caldin and Long,[2] have shown that catalysis of the protonation of 2,4,6-trinitrobenzyl anion (TNT$^-$) by several substituted acetic acids gives an α value of 0.5 at 20° in a typical Brønsted catalysis plot. More recently, Blake, Evans, and Russell[4] have studied the catalysis of the same anion by phenols and give a value of 0.84 ± 0.07 for α (at −40°). In the present paper we attempt to give a more detailed description of the behavior of the catalysis coefficient with the acid strength of the catalyzing acid for 2,6-dinitrobenzyl anion and correlate it with the data of 2,4,6-trinitrobenzyl anion in the light of the comprehensive description of acid–base catalysis given by Eigen and coworkers.[9,10]

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(1) E. F. Caldin and E. Harbron, *J. Chem. Soc.*, 3454 (1962).

(2) E. F. Caldin and G. Long, *Proc. Roy. Soc.*, **A228**, 263 (1955).

(3) E. F. Caldin and M. Kasparian, *Discussions Faraday Soc.*, **39**, 25 (1965).

(4) J. A. Blake, M. J. B. Evans, and K. E. Russell, *Can. J. Chem.*, **44**, 119 (1966).

(5) J. D. Margerum, *J. Am. Chem. Soc.*, **87**, 3772 (1965).

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(7) G. Wettermark, *J. Phys. Chem.*, **66**, 2560 (1962).

(8) G. Wettermark and R. Ricci, *J. Chem. Phys.*, **39**, 1218 (1963).

Table I. Data for Reaction of 2,6-Dinitrotoluene Anion with Various Donor Acids

No.	HA (donor acid)	pK_{HA}	ΔpK (pK_{DNT}[a] − pK_{HA})	k_{HA} (30°), l. mole^{-1} sec^{-1}	Log k_{HA}	Measured pH[b]	Intercept, $k_{H^+}[H^+]$ + $k_{H_2O}[H_2O]$, sec^{-1}	Log intercept
1	H_3O^+	−1.75	20.75	1×10^5	5.00			
2	$CH_2(COOH)_2$	2.86	16.14	4.39×10^4	4.64	2.17	4.51×10^2	2.65
3	$ClCH_2COOH$	2.87	16.13	3.15×10^4	4.50	2.37	4.50×10^2	2.65
4	$BrCH_2COOH$	2.90	16.10	3.74×10^4	4.57	2.28	3.56×10^2	2.55
5	$(COOH)CH_2C(OH)(COOH)CH_2COOH$	3.13	15.87	7.10×10^4	4.85	2.27	4.23×10^2	2.63
6	CH_3OCH_2COOH	3.53	15.47	2.31×10^4	4.36	2.78	1.48×10^2	2.17
7	$(-CH_2COOH)_2$ (10:1)	4.21	14.79	2.66×10^4	4.26	2.59	1.95×10^2	2.27
	(1:1)			3.35×10^4	4.52	3.36	5.0×10^1	1.75
8	CH_3COOH	4.74	14.26	9.97×10^3	4.00	4.1	2.6×10^1	1.42
9	$^-OOC(CH_2)_3COOH$	5.27	13.73	1.08×10^4	4.03	4.43	1.95×10^1	1.29
10	$^-OOCCH_2COOH$	5.70	13.30	3.98×10^3	3.60	5.0	1.25×10^1	1.10
11	$H_2PO_4^-$ (10:1)	7.21	11.79	2.7×10^3	3.43	6.1	1.5×10^1	1.18
12	$^+HN(CH_2CH_2OH)_3$	7.7	11.30	4.99×10^3	3.70	9.58	8.7	0.94
13	$^+H_2N(CH_2CH_2OH)_2$ (10:1)	8.88	10.12	4.4×10^3	3.64	7.43	10.0	1.00
	(1:1)			4.16×10^3	3.62	8.67	9.0	0.95
14	$^+H_3NCH_2CH_2OH$	9.50	9.50	7.06×10^2	2.85	8.13	9.5	0.98
15	H_2NCH_2COOH	9.78	9.22	5.64×10^2	2.75	9.95	10.0	1.00
16	HPO_4^{2-}	11.71	7.29	1.13×10^1	1.05	10.37	8.62	0.94
17	H_2O	15.74	3.26	1.6×10^{-1}	−0.79			
18	D_2O	16.5	2.50	2.35×10^{-2}	−1.63			

[a] pK of 2,6-DNT = 19.0 (ref 13). [b] Solutions 1 M in $NaClO_4$.

Experimental Work

Preparation of Solutions. Stock solutions of 1:1 ratio (except where otherwise specified) of buffer acid to sodium salt of the buffer were prepared either by titration of the acid with one-half the equivalent amount of standard sodium hydroxide or by direct dissolution of the acid and salt in water. The acids were previously purified by recrystallization or fractional distillation.

Solutions for kinetic study were prepared from a stock solution of 2,6-dinitrotoluene (2,6-DNT) in ethanol. The final solutions were 2×10^{-4} M in 2,6-DNT, 1% in ethanol, and 1 M in sodium perchlorate to maintain essentially constant ionic strength. For each buffer system studied, six solutions spanning a buffer acid concentration range of 5×10^{-2} to 5×10^{-3} M were used. A Beckman Model G pH meter was used to measure the pH of all solutions.

The solution in D_2O was prepared with KOD and D_2O (99.8% from Volk Radiochemical) and a weighed sample of 2,6-DNT to avoid exchangeable hydrogen.

Flash Apparatus and Rate Measurements. The flash apparatus has been previously described.[11] An 1800-J (20 kV, 9 μf) flash of 8 μsec ($1/e$ time) duration was used to generate the transient species. The solutions were thermostated at 30° and from 15 to 80° for the activation energy determination by circulating water through the outer jacket of the 20-cm quartz cell. The spectra of the transients were obtained by plotting the absorbance ($\log I_\infty/I_t$ at a given time t after flash *vs.* wavelength). The pseudo-first-order rate constants, k_{exptl}, were determined by a least-squares analysis of the log absorbance *vs.* time plots.

Results

The plots of log absorbance *vs.* time were linear and yielded pseudo-first-order rate constants, k_{exptl}, for all solutions at all pH's and buffer concentrations. Earlier experiments[8,12] showed k_{exptl} to be dependent on buffer acid concentration, on pH, and on the solvent as would be expected of a species showing general acid catalysis. Thus, the contribution of each of these components to the over-all rate was determined in the following manner.

For any given buffer acid, HA, the values of k_{exptl} at six different concentrations of buffer were plotted *vs.* buffer acid concentration. At each concentration of buffer, the value of k_{exptl} used was the average of nine separate determinations. The standard deviation for the determination of k_{exptl} was of the order of 0.21. The least-squares analysis of the linear plot gave a slope of k_{HA} and an intercept representing the hydrogen ion and solvent terms.

$$k_{exptl} = k_{HA}[HA] + k_{H_3O^+}[H_3O^+] + k_{H_2O}[H_2O]$$

The values of log k_{HA} are given in Table I.

The log of the intercepts are shown plotted *vs.* pH in Figure 1 along with data from perchloric acid and sodium hydroxide solutions. At a pH below 1.5, a limiting rate of 2×10^3 sec^{-1} is reached. Between pH 2 and 3 the slope of the curve is minus unity indicating a direct dependence of the rate on proton concentration. Above pH 6 a limiting rate of 0.95 sec^{-1} is reached. The latter limiting rate gives the contribution of water acting as an acid, in the absence of all other catalysts, $k_{H_2O}[H_2O]$. When divided by the molarity of water, it gives k_{H_2O}. Likewise, k_{D_2O} was determined from the limiting rate in D_2O solutions of KOD. Extrapolation of the minus unity portion of the curve to pH 0 gave the value of log k corresponding to $k_{H_3O^+}$ since the contribution due to catalysis by H_2O is negligible at low pH. The value of $k_{H_3O^+}$ can also be determined from the perchloric acid data in Figure 1 by plotting k_{exptl} *vs.* $[HClO_4]$. The slope of such a plot yields $k_{H_3O^+} = 5.2 \times 10^5$ l. mole^{-1} sec^{-1}.

The limiting value of the rate of disappearance of transient at low pH shown in Figure 1 is considered to be the rate of tautomerism from the *aci* to the *nitro* form. The absorption spectrum of the transient in this pH region is shown in Figure 2 and is different from that of the anion at higher pH.

Activation energies, ΔE_*, were determined for the *aci* → nitro tautomerism in 1.8 M $HClO_4$ and for the anion → nitro reaction in 0.1 M NaOH and are 10.1 and 11.5 kcal mole^{-1}, respectively. These were determined by a least-squares analysis of an Arrhenius plot from rate data obtained at six temperatures from 15 to 80°.

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(10) M. Eigen, W. Kruse, G. Maass, and L. deMaeyer *Progr. Reaction Kinetics*, 2, 287 (1963).

(11) L. Lindqvist, *Rev. Sci. Instr.*, **35**, 993 (1964).

(12) G. Wettermark, E. D. Black, and L. Dogliotti, *Photochem. Photobiol.*, **4**, 229 (1965).

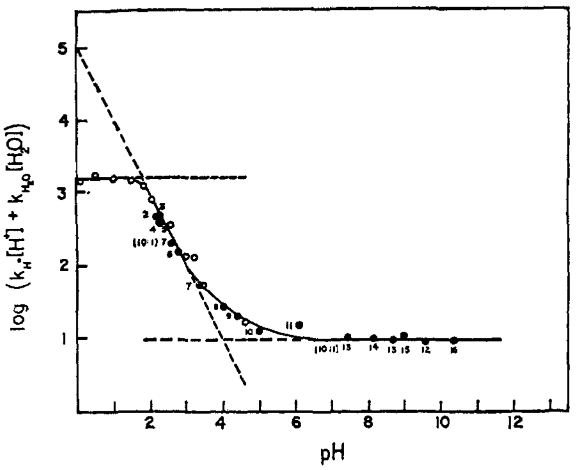

Figure 1. The logarithm of the rate constant at 30° for the fading reaction of 2,6-dinitrobenzyl anion as a function of pH. O's refer to solutions at various concentrations of perchloric acid. ●'s refer to the intercepts of plots of k_{exptl} *vs.* buffer acid concentration. The numbers refer to the corresponding donor acid in Table I. (10:1) signifies the buffer ratio [HA]/[A⁻]. All other values were for a buffer ratio of 1:1.

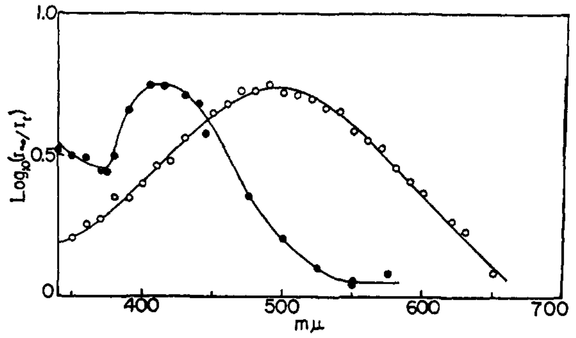

Figure 2. Optical absorption spectra of transients produced immediately after flash from aqueous solutions of 2,6-dinitrotoluene: ●, spectrum produced in 1 *M* $HClO_4$; O, spectrum produced in 0.1 *M* NaOH.

Discussion

Recent use of relaxation techniques to study acid- and base-catalyzed reactions has considerably broadened the spectrum of rates over which some systems could be studied. New light has thus been cast on the mechanisms of proton-transfer reactions, particularly in aqueous solution. Eigen and coworkers have done extensive studies on general acid catalyzed reactions that have emphasized the fact that α in the Brønsted relation, $k_{HA} = G_{HA}K_{HA}\alpha$, is not a constant, but may vary continuously from values of one to zero as the pK_{HA} of the donor acid is decreased. Former assumptions of linear behavior, *i.e.*, constant α, were based upon a McLaurin expansion of the Brønsted expression to give the straight-line form

$$\log k_{HA} = \alpha pK + C$$

and as such must be recognized as valid only over very small p*K* ranges.

When log k_{HA} is plotted *vs.* the difference in p*K* between the donor and acceptor acids (Δp*K*), a curve depicting the variance of α from one at low Δp*K* to zero at high values of Δp*K* is obtained for simple general acid catalysis reactions.[9] Such a curve is obtained for the 2,6-dinitrotoluene anion fading reaction when the values of log k_{HA} in Table I are plotted *vs.* Δp*K* (see Figure 3). The thermodynamic p*K* of the 2,6-DNT was taken as 19.0.[13,14]

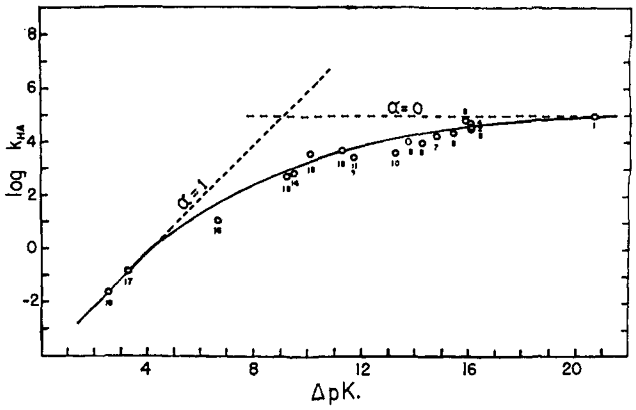

Figure 3. The logarithm of the rate constant for the reaction of donor acid, HA, with 2,6-dinitrobenzyl anion *vs.* Δp*K* [pK_a (acceptor) − pK_a(donor)]. Numbers correspond to the donor acids listed in Table I.

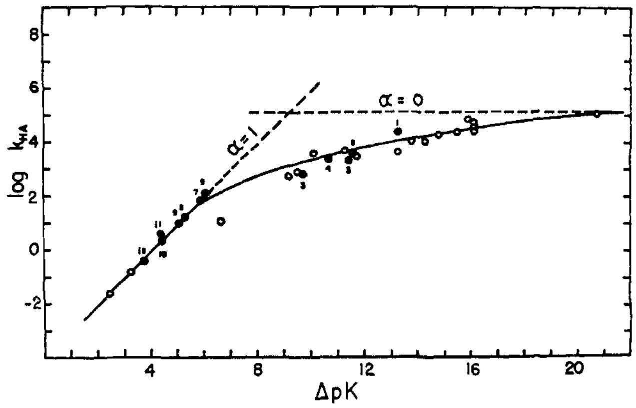

Figure 4. The logarithm of the rate constant for the reaction of nitrobenzyl anion with various donor acids *vs.* Δp*K*: ●, reaction with 2,4,6-trinitrobenzyl anion in ethanol at 30° (numbers refer to donor acids listed in Table II); O, reaction with 2,6-dinitrobenzyl anion.

When the Arrhenius data given by Caldin and coworkers[1-3] and Russell, *et al.*,[4] for 2,4,6-trinitrobenzyl anion in ethanol are used to calculate values of log k_{HA} at 30° (see Table II) and these values are plotted *vs.* Δp*K*, the data fit on the same curve as those for 2,6-dinitrobenzyl anion (see Figure 4). The solvent does not appear to make any significant difference, and the transfer of the proton between acid and anion may occur directly without any intervening solvent molecules.

The curve illustrates some interesting deviations from "ideal" behavior and in so doing sheds light on the nature of the proton-transfer process. One normally expects proton-transfer processes to be diffusion controlled, *i.e.*, $k_{HA} \rightarrow 10^{10}$ l. mole^{-1} sec^{-1} as Δp*K* becomes large. In this case, however, the limiting value as $\alpha \rightarrow 0$ appears to be about 10^5 or 10^6 l. mole^{-1} sec^{-1}. Similar behavior has been shown to be the case for other molecules like barbituric acid and Meldrum's acid whose conjugate bases exist as carbanions which

[13] R. Schaal, *Compt. Rend.*, **239**, 1036 (1954).

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Table II. Data for Reaction of 2,4,6-Trinitrotoluene Anion with Various Donor Acids

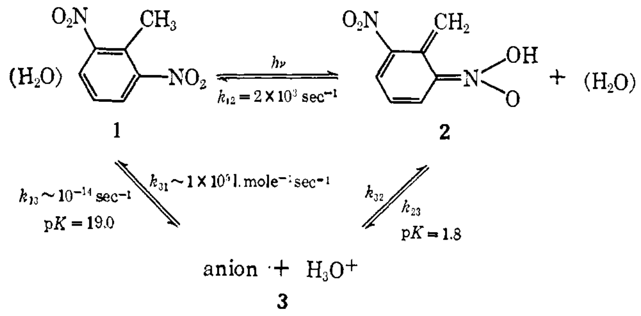
No.	Donor acid	pK_{HA}	ΔpK ($pK_{TNT}{}^a$ − pK_{HA})	ΔE_A, kcal/mole	Log A	Ref for Arrhenius data	Calcd log k_{HA} (30°)
1	$CHCl_2COOH$	1.25	13.20	8.5	10.50	2	4.38
2	$CH_2ClCOOH$	2.86	11.59	8.23	9.48	1	3.55
3	HF	3.0	11.45	11.1	11.3	3	3.30
4	$CH_2(OH)COOH$	3.82	10.63	9.6	10.30	2	3.38
5	CH_3COOH	4.74	9.71	9.38	9.55	1	2.79
6	3-NO_2-phenol	8.40	6.05	10.9	9.96	4	2.11
7	3-CN-phenol	8.61	5.84	10.9	9.69	4	1.84
8	3-$COCH_3$-phenol	9.19	5.26	10.1	8.51	4	1.23
9	4-Cl-phenol	9.38	5.07	10.0	8.20	4	1.00
10	Phenol	9.98	4.47	9.4	7.20	4	0.434
11	3-CH_3-phenol	10.08	4.37	9.8	7.64	4	0.584
12	3-CH_3-phenol-d_1	10.69[b]	3.76	...	...	...	0.416[c]

[a] pK_{TNT} = 14.45, ref 13. [b] Reference 14. [c] Calculated from isotope effect reported in ref 4.

are stabilized by delocalization of charge.[15] In such cases the slow rate of proton transfer is considered to be due to two interrelated factors: (1) hydrogen bonds of the type $RH_2C^- \cdots H^+—A^-$ by which proton is transferred directly from acid to base do not form easily, and thus the amount of H-bonded species is small and the apparent rate of reaction slow; (2) the proton transfer requires a large charge displacement in going from the resonance stabilized anion to the neutral molecule.

In the pH region of 3–2 an increasing amount of anion must disappear *via* protonation to the thermodynamically less stable *aci* form followed by rearrangement to the more thermodynamically stable nitro form.

Two factors prevented determination of either k_{23}, the rate of proton transfer from *aci* to solvent, or k_{32}, the rate of proton transfer to anion to give the *aci* form. (1) The time resolution of our instrument does not allow us to watch the formation of anion from the photoformed *aci* tautomer in aqueous solutions, *i.e.*, the pseudo-first-order rate must be greater than 4 × 10^5 sec^{-1}. (2) The rate-determining step for the disappearance of anion *via* the *aci* species is not protonation of the anion to give *aci* (k_{32}), but the following step, *viz.*, *aci* rearranging to nitro (k_{21}).



One would expect, in analogy with protonation of the enol forms of barbituric acid and Meldrum's acid, that the rate of protonation of anion at the nitro group would occur at least one to two orders of magnitude faster than protonation at carbon. This is because transfer of proton through hydrogen bonds of the type $O—H^+ \cdots {}^-O–$ is normally much faster than those of the type $O—H^+ \cdots {}^-C–$.[9] Temperature-jump experiments in the pH region 1.8–2.8 may allow one to determine the rate of dissociation of the *aci* tautomer, k_{23}, directly. Then, of course, k_{32} may be determined from the dissociation constant K given here.

We should like to point out the possible danger of making straight-line extrapolations of Brønsted plots over too large a pK_a range. One such extrapolation[16] in a polarographic study of phenylnitromethane gave a value of $k_{H_3O^+}$, much too high for the protonation of phenylnitromethane anion. This led the authors to the unfortunate conclusion that the anion exists in two forms and that the rate-determining step in protonation of the nitro form is the conversion of *aci* anion to *nitro* anion.

Acknowledgment. The authors wish to thank Dr. Manfried Eigen for his helpful discussion of our results.

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